

INVESTIGATIONS OF CORE-HOLE EFFECTS IN X-RAY AND AUGER SPECTRA OF SIMPLE METALS

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the Final State Rule.

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Abstract

The dynamical theory of x-ray spectra due to Nozieres and DeDominicis (ND) is here evaluated numerically for numerous model systems including cases where the core-hole potential possesses a bound state. It is shown that the resulting emission spectra obey the Final State Rule rather accurately. An approximate but analytical derivation of this rule is given which provides insight into the mechanisms leading to the Final State Rule. The evaluations are performed using two methods, one based on an integral equation and a separable core-hole potential and the other based on determinantal wave functions for a finite number (N) of electrons in a box. The equivalence of the two methods are demonstrated both formally and numerically. By comparing them we prove the finite- N approach to be accurate already for rather small N . We also show that a separable potential does not give rise to any spurious results but can actually be chosen to yield the same ND spectrum as a local potential. ND theory

of XPS is discussed and from calculations of the exponent function $\alpha(\omega)$ for several model systems closely corresponding to simple metals we conclude the equivalence of this theory to its asymptotic approximation as far as the extraction of asymmetry indices is concerned. Recent criticism of the major conclusions reached here and in previous work is refuted.

1. Introduction.

The present paper is devoted to a discussion of current theories of x-ray spectra with regard to their capability of yielding quantitative predictions for experiments on simple metals. We will mainly be concerned with the overall shapes of x-ray emission and absorption spectra but will also discuss the threshold singularities and the related line-shape of x-ray photoemission (XPS) spectra from core levels.

Until very recently all quantitative calculations of x-ray spectra of metals were based on a one-particle approach in which the x-ray transition is viewed as occurring between a core orbital and a valence Bloch state of the perfect crystal. This simple approach is known to give an accurate description of the experimental emission spectra¹⁻⁴ and if the one-particle result is also amended with a multiplicative power-law singularity and broadened, the agreement with experiment becomes almost perfect⁵⁻⁷. Thus, the fact that there is a strong perturbing potential due to the presence of a core hole in the initial state of the emission process seems to have a very small effect on the shape of the x-ray spectrum except close to threshold. Within a one-particle approach it would have been equally justified to picture the x-ray transition as taking place between a core orbital and a valence state which is obtained in the one-particle potential which incorporates

both the periodic solid and the screened core hole. We know now^{9,6} that such a picture results in emission spectra which have very little resemblance to experimental spectra in simple metals.

In the case of x-ray absorption spectra, which probe the unoccupied valence states, there is not such a drastic difference between the two one-particle approaches - that neglecting the hole (the band case) and that accounting for the hole (the impurity case). Also, there exist no accurate calculations of x-ray absorption spectra in simple metals based on the impurity approach. Therefore, in these systems, there is not yet enough empirical evidence for preferring one approach over the other. In atoms, however, it is well known¹⁰ that a one-particle approach will give reasonable photoabsorption cross-sections only if the outgoing electron is allowed to feel the potential from the fully relaxed (screened) hole left behind.

Guided by the empirical facts presented above¹¹, the present authors were led to the Final State Rule^{13,9} according to which accurate emission and absorption spectra of simple metals can be obtained from a simple one-particle approach provided the transition matrix elements are calculated from wave functions obtained in the potential of the final state of the x-ray process, i.e. with the core hole in absorption and without the core hole in emission. The Final State Rule also states that¹⁴ even the singular behavior of the spectra near threshold

can be accurately described by multiplying the one-particle result with power-law factors, one for each of the angular momentum channels contributing to the spectrum. Thus, the Final State Rule exactly corresponds to the commonly used procedure for interpreting experimental spectra^{5,15-20}.

As mentioned previously, there now exists an overwhelming amount of experimental information in support of the Final State Rule. However, in order to explain the rule from basic theory one clearly must go beyond the one-particle formalism and incorporate the basic dynamics of the x-ray process, namely that a very strong perturbation due to the core hole is switched off (on) in the emission (absorption) process. The simplest possible theory which accounts for this switching is due to Nozières and DeDominicis¹² (ND). It is well known, that this theory gives a definite prediction for the shape of edge singularities in x-ray and XPS spectra. More importantly, however, the ND theory provides an answer for the overall shape of the main band of these spectra. We have previously^{9,14} evaluated this theory numerically for model systems which were chosen to correspond closely to real simple metals. We then found that the resulting spectra were accurately described²¹ by the Final State Rule. We later evaluated the ND theory for other model systems including systems with very strong core-hole potentials. We also used different numerical methods and the results are unambiguous. As a matter of fact, to this date, no case is known for which the solution to the ND theory does

not obey the Final State Rule rather accurately. Since the Final State Rule is in accord with experiment, so is the ND theory, which could be considered to be somewhat surprising in view of the fact that this theory does not account for the interactions between the valence electrons other than in the static screening of the core hole potential. Dynamic screening is e.g. not taken into account. It should, however, be remembered that the agreement between ND theory and the Final State Rule or experiment, although rather good, is only approximate and there is still room for modifications due to core-valence exchange and the valence-valence interactions.

In retrospect the Final State Rule seems to be a rather trivial restatement of basic facts. Nevertheless, the rule seemed to be rather controversial at the time it was suggested¹³. Several workers had actually proposed what would be equivalent to an initial state rule for emission²⁴⁻²⁶ and also for absorption²⁷. These investigations were based on rather crude models which could perhaps explain the somewhat curious conclusions. More serious, however, is the fact that the Final State Rule was challenged in a recent Physical Review Letter²⁸ presenting an investigation which was also based on the ND theory. In this work Swarts, Dow, and Flynn evaluated the ND theory for several model cases using a method first discussed by Friedel²⁹ and later used by Kotani and Toyozawa³⁰. The method is based on Slater determinants for a finite number of electrons in a box. Swarts et al. then claimed that their results for moderately strong core hole

potentials were rather well described by one-particle theory using wave functions obtained in the presence of the core hole, i.e. by an initial state rule in the case of emission. For stronger potentials they claimed that the spectra could not be described by either an initial-state or a final-state rule, using the terminology introduced above. Thus, these conclusions of Swarts et al. are in clear contradiction to our claim that the ND theory satisfies the Final State Rule. Swarts et al. consequently questioned the widespread procedure implicitly based on the Final State Rule and used by many workers^{5,15-20} in order to interpret their experimental spectra and extract threshold exponents. It would be a quite serious matter if these objections were justified. The critique by Swarts et al. is, however, based on a misinterpretation of the obtained results. It is the purpose of this paper to show beyond any reasonable doubt that the ND theory does indeed obey the Final State Rule rather accurately.

Our earlier evaluations of the ND theory were based on the integral-equation formulation originally introduced by Nozières and DeDominicis, which is simplified considerably by the use of a separable potential. We will show here both formally and numerically, that this method is equivalent to the determinantal, finite-N approach used by Kotani and Toyozawa^{29,30}. In fact, with only 80 s-waves in a box, the latter approach gives the same spectrum as the former within the experimental uncertainties. We will also show that realistic systems may be modeled satisfactorily by using separable core hole potentials.

For instance, a square well potential and a separable potential give nearly identical ND (dynamical) spectra provided the parameters of the separable potential are chosen so as to make the static initial-state spectra agree as closely as possible. In particular, the Fermi level phaseshifts and the integrated intensities should be chosen equal. In this paper we also offer further illustrations to the numerical accuracy of the Final State Rule in comparison with the ND theory. We will e.g. present results for cases where the core-hole potential is strong enough to pull a bound state out of the continuum. We will here only present results for emission because the static influence of the core hole is in this case much more drastic than in the case of absorption. For the Final State Rule in absorption we refer to Ref. 14. The calculations presented in this paper were carried out using both the integral-equation formulation and the finite-N approach. In particular, we repeated several of the calculations by Swarts et al. to demonstrate that the resulting spectra do indeed obey the Final State Rule rather accurately.

Given the accuracy of the Final State Rule it would be desirable to have an explanation for the rule in simple physical terms. What we offer in this regard is only an approximate treatment within the finite N approach, which can be solved analytically and which leads naturally to the Final State Rule. This analysis also shows that the "excitonic" part of the singularity³¹ is approximately multiplicative in frequency space. That part of the

singularity which is due to the Anderson orthogonality catastrophe³² and which is known to be multiplicative in time space (a convolution in frequency space) is, however, lost in this approximation.

The shape of the main line in photoemission spectra from core levels is rather accurately described in terms of the one-core-hole spectral function³³. As mentioned above, ND theory offers a definite prediction $A_{ND}(\omega)$ for this quantity. Since there is no valence-valence interaction in the ND theory, $A_{ND}(\omega)$ does not have the correct satellite structure e.g. due to plasmon production. It is, however, believed^{33,34} that $A_{ND}(\omega)$ provides a rather accurate description of the asymmetric main XPS line. The spectral function of the ND theory behaves asymptotically as a power-law singularity $C \cdot \omega^{(\alpha-1)}$ for energies ω very close to the core electron binding energy. This behavior with the same exponent α is generally believed^{33,35} to be correct also for fully interacting electrons. This fact forms the basis for the theoretical interpretation of the experimental XPS lines which are fitted by a broadened version of the asymptotic line shape $C \cdot \omega^{(\alpha-1)}$ ³⁶⁻³⁸. In this way, the core-electron binding energy, the core-hole life time, the phonon broadening, and the asymmetry index α can be extracted from experiment.

The spectral function of ND theory, A_{ND} , obeys the sum rule $\int A_{ND}(\omega) d\omega = 1$, which expresses the fact that there must be unit probability for finding the remaining

system either in the ground state or in some excited state after the XPS process. Now clearly, the asymptotic spectrum ($C \cdot \omega^{(\alpha-1)}$) does not obey this sum rule since the corresponding frequency integral diverges. Therefore, it is a mathematically correct but vacuous statement to say that the ND-spectral function (A_{ND}) deviates from the asymptotic spectrum away from threshold ($\omega \neq 0$). Nevertheless, Dow and Flynn³⁹ and Bowen and Dow⁴⁰ have recently criticized the experimental procedure discussed above on precisely this ground. In this paper we will address the more relevant physical question: how large are the errors in the experimentally extracted broadenings and asymmetry indices, that are introduced by using the asymptotic line-shape rather than the full result of ND theory. This question we answer by computing $A_{ND}(\omega)$ for model systems relevant to real simple metals, applying both Lorentzian and Gaussian broadening to the result and, finally, by trying to retrieve the input parameters (broadenings and asymmetry index α) through the fitting procedure mentioned above³⁶⁻³⁸. In all cases we find the errors to be smaller than the corresponding experimental uncertainties. We can thus say with confidence that ND theory is equivalent⁴¹ to its asymptotic version in simple metals.

From this investigation we can, however, not say anything about the relevance of ND theory to real x-ray or x-ray photoemission spectra. For this we must rely on a comparison with experiment or on a deeper theoretical analysis which also accounts for the valence-valence

interaction. There is, however, presently no experimental^{5,15-20,36-38}, or theoretical³⁴ⁿ reason to expect that the results of ND theory would be substantially altered by taking this interaction into account - at least not as far as the main features of x-ray and x-ray photoemission spectra are concerned.

2. Theory of SXE and computational details.

The determinantal approach^{29,30} and the integral-equation formulation¹² represent two exact ways of solving the same problem. This equivalence will be demonstrated explicitly in this section. The integral-equation formulation was derived by Nozieres and DeDominicis using the diagrammatic technique of many-body perturbation theory which makes their work less easily accessible than the conceptually simpler determinantal approach. Following the work by Langreth⁴², we will here present an elementary but nevertheless exact derivation which assumes no familiarity with Green's-function techniques. In this section we will also give some theoretical and computational details which are needed in order to understand how the results presented in Sec. 5 were obtained.

We start with the Golden Rule expression for the x-ray emission intensity $I(\omega)$

$$I(\omega) = \sum_f |\langle f | T | i \rangle|^2 \delta(\omega + E_f - E_i) \quad (2.1)$$

The full expression also involves a slowly varying factor $C\omega$ which has its origin in the photon degrees of freedom, but for simplicity this factor will be omitted here. It must, of course, be included before comparing to

experiment. As we will here only present emission intensities our formulae will only pertain to this case, but the case of absorption represents no additional difficulties. The initial state $|i\rangle = |N\sim\rangle$ of the emission process is assumed⁸ to be the quasi-ground state of N valence electrons in the presence of the core hole, i.e. $c^+c|N\sim\rangle = 0$, where the operator c annihilates a core electron, and we write the energy of this state as $E_i = E_0(N)$. The possible final states $|f\rangle = c^+|N-1,s\rangle$ are excited states (s) of $N-1$ valence electrons, the core orbital being occupied. The energies of these states are written as $E_f = E_s(N-1) + \epsilon_c$ where ϵ_c is the unrelaxed (e.g. Hartree-Fock) core-electron energy. The operator T , responsible for the x-ray transition, is, in the dipole approximation, given by

$$T = \sum_k p_{ck} c^+ a_k \quad (2.2)$$

where $p_{ck} = \langle c|p|k\rangle$ is the one-particle dipole matrix element and where k labels a set of annihilation operators (a_k) corresponding to a complete orthonormal set ($\phi_k(r)$) of one-particle valence orbitals. From the assumption above we have $cc^+|N\sim\rangle = |N\sim\rangle$ giving a transition matrix element

$$\langle f|T|i\rangle = \sum_k p_{ck} \langle N-1,s|a_k|N\sim\rangle \quad (2.3)$$

At this stage it is convenient to introduce the (unnormalized) transition-state orbital

$$\psi_b(r) = \sum_k p_{ck}^* \psi_k(r) \quad (2.4)$$

and the corresponding annihilation operator

$$b = \sum_k p_{ck} a_k \quad (2.5)$$

We also define the Fermi level $\epsilon_F = E_O(N) - E_O(N-1)$, the shift $\Delta = E_O(N) - \tilde{E}_O(N)$, giving the lowering of the total energy of the valence electrons upon introduction of the core-hole potential, the energy of the quasi-hole $E_c = \epsilon_c + \Delta$, i.e. the core-electron binding energy, and the excitation energies $\omega_s = E_s(N-1) - E_O(N-1)$ of the system of $N-1$ valence electrons. The shift Δ contains a term $\langle N|V|N \rangle$ which is linear in the core-hole potential V . The sum of the remaining terms, Δ_r , is equal to $\Delta + \langle N|V|N \rangle = \langle N|\tilde{H}|N \rangle - \langle N|\tilde{H}|N \rangle$ and, due to the variational principle, this sum only contains second and higher order terms in the potential. Therefore, Δ_r is usually referred to as a relaxation shift⁴³. Thus

$$\Delta = \Delta_r + \langle N|V|N \rangle \quad (2.6)$$

With these definitions, energy conservation, imposed by the δ -function in Eq. (2.1), leads to the intuitively obvious result $\omega = \epsilon_F - E_c - \omega_s$, which, as $\omega_s > 0$, restricts the emission spectrum to lie below a threshold given by $\epsilon_F - E_c$. Defining a shifted spectrum $J(\omega) = I(\omega - E_c)$ with the threshold at the Fermi level, $\omega = \epsilon_F$, we obtain

$$J(\omega) = \sum_s |\langle N-1, s | b^+ | N \rangle|^2 \delta(\omega + \omega_s - \epsilon_F) \quad (2.7)$$

So far, the discussion has been quite general but in order to proceed we must take advantage of the basic assumption of ND theory, namely that the valence electrons are scattered by the core-hole potential V in the initial state but do otherwise not interact in either initial or final state. Thus, they are described by the non-interacting Hamiltonians

$$\tilde{H} = \sum_k \epsilon_k a_k^+ a_k + \sum_{k,k'} V_{kk'} a_k^+ a_{k'} \quad (2.8)$$

and

$$H = \sum_k \epsilon_k a_k^+ a_k \quad (2.9)$$

in the initial state and final state, respectively. The energies ϵ_k are the usual band energies of the perfect solid. In terms of the annihilation operators $\tilde{a}_k$, corresponding to the one-particle basis set $\{\tilde{\psi}_k(\underline{r})\}$ which is obtained in the presence of the core hole and which thus diagonalizes $\tilde{H}$, these non-interacting Hamiltonians can, of course, also be written

$$\tilde{H} = \sum_k \tilde{\epsilon}_k \tilde{a}_k^+ \tilde{a}_k \quad (2.10)$$

$$H = \sum_k \tilde{\epsilon}_k \tilde{a}_k^+ \tilde{a}_k - \sum_{k,k'} \tilde{V}_{kk'} \tilde{a}_k^+ \tilde{a}_{k'} \quad (2.11)$$

From this basic assumption it follows that the state $|N\sim\rangle$, the ground state of $\tilde{H}$, is just a Slater determinant made up of the N lowest orbitals $\tilde{\psi}_k(r)$. Furthermore, the states $|N-1,s\rangle$ are eigenfunctions of H and can be generated from the ground state Slater determinant $|N-1\rangle$ by creating all possible single and multiple particle-hole pair excitations. Choosing latin (greek) letters to indicate orbitals below (above) the Fermi level, we obtain the series of determinantal states

$$|N-1\rangle \text{ (with energy } E_0(N-1) = \sum_k^{N-1} \epsilon_k),$$

$$a_\mu^+ a_k |N-1\rangle \text{ (with energy } E_0(N-1) + \epsilon_\mu - \epsilon_k),$$

$$a_\nu^+ a_\mu^+ a_k a_\lambda |N-1\rangle \text{ (with energy}$$

$$E_0(N-1) + \epsilon_\nu + \epsilon_\mu - \epsilon_k - \epsilon_\lambda), \text{ etc.}$$

Consequently, we find

$$J(\omega) = |\langle N\sim | b^+ | N-1 \rangle|^2 \delta(\omega - \epsilon_F)$$

$$+ \sum_{\mu,k} |\langle N\sim | b^+ a_\mu^+ a_k | N-1 \rangle|^2 \delta(\omega + \epsilon_\mu - \epsilon_k - \epsilon_F)$$

$$+ \sum_{\mu,\nu,k,\lambda} \dots \quad (2.12)$$

Obviously, the states $b^+ |N-1,s\rangle$ are also Slater

determinants and, therefore, all matrix elements appearing in Eq. (2.12) are simple scalar products of determinantal wave functions. Such a product is easily seen to yield the determinant of the overlap matrix of the corresponding one-particle orbitals. With a finite number (N) of valence electrons in a box, one obtains a finite level spacing between the one-particle energies ϵ_k , but replacing the δ -functions in Eq. (2.12) by normalized Gaussians with a width somewhat larger than this spacing, a continuous emission spectrum $J(\omega)$ is obtained from Eq. (2.12) by specifying the dipole matrix elements p_{ck} and the one-particle overlap integrals $\langle \tilde{\phi}_k | \phi_k \rangle$. The evaluation of the first term in Eq. (2.12) requires of the order of N^3 elementary arithmetic operations. As a by-product of this evaluation one obtains the so-called minors of the determinant $\langle N-1 | b^+ | N-1 \rangle$, from which each term (μ, k) in the sum of the second term is obtainable by ca. N operations. Summing over a set of orbitals ϕ_μ also chosen to be of order N , the computation of the contribution from the single pair excitations, i.e. the second line of Eq. (2.12), is again an N^3 -operation. The double pair excitations, i.e. the third line in Eq. (2.12), however, present a problem of order N^4 , and higher excitations become exceedingly more time-consuming. With an increasing number (N) of electrons, i.e. with a decreasing level spacing, these higher excitations contribute a larger and larger fraction of the total emission intensity, eventually rendering the determinantal approach intractable. Fortunately, it is possible to find an N (ca. 100) such that almost all intensity is given by single

pair excitations and such that the shape of the resulting spectrum is very close to the spectrum obtained in an infinite system ($N \rightarrow \infty$). This is a somewhat unexpected result for which we have no simple physical explanation, but which nevertheless makes the determinantal approach a very convenient way to evaluate the ND theory. All emission results from this approach presented in the present work were obtained by including only single pair excitations, i.e. by truncating the expansion on the right hand side of Eq. (2.12) after the second term. In Fig.

1 we compare the result of the determinantal approach using 80 s-electrons in a box with the corresponding result for the infinite system obtained from the integral equation to be derived below, and the agreement is indeed striking.

The convergence of the determinantal approach with respect to N towards the limit of a very large system can also be studied from the sum rule obeyed by the integrated emission intensity. This quantity is easily obtained from Eq. (2.7) by using the completeness of the states $|N-1, s\rangle$

$$\int_{-\infty}^0 J(\omega) d\omega = \langle N\sim | b^\dagger b | N\sim \rangle \quad (2.13)$$

By expressing the operator b in terms of the basis set $(\tilde{\psi}_k)$ obtained in the presence of the core hole (c.f. Eq. (2.5)), the right hand side of Eq. (2.13) becomes $\sum_{k,k'} \langle N\sim | \tilde{a}_k^\dagger \tilde{a}_{k'} | N\sim \rangle \tilde{p}_{ck}^* \tilde{p}_{ck}$, and consequently, from the definition of the quasi-ground state $|N\sim\rangle$,

$$\int_{-\infty}^0 J(\omega) d\omega = \sum_k^{\text{occ}} |\tilde{p}_{ck}|^2 \quad (2.14)$$

where "occ" indicates that the sum extends over the N lowest orbitals $\tilde{\phi}_k$. At this stage it is convenient to introduce two other concepts central to our discussion - the static initial-state spectrum, $J_i(\omega)$, and the static final-state spectrum, $J_f(\omega)$. These are defined as the shifted spectra obtained within simple one-particle theory with core-valence dipole matrix elements computed from valence orbitals obtained in the presence of the core hole and in the absence of the hole, respectively. Thus

$$J_i(\omega) = \sum_k^{\text{occ}} |\tilde{p}_{ck}|^2 \delta(\omega - \epsilon_k) \quad (2.15)$$

$$J_f(\omega) = \sum_k^{\text{occ}} |p_{ck}|^2 \delta(\omega - \epsilon_k) \quad (2.16)$$

and the sum rule (Eq. (2.14)) then shows that the integrated intensity of the dynamical spectrum $J(\omega)$ is equal to that of the static initial state spectrum. When only single-pair excitations are included in the dynamical spectrum, its integrated intensity does not exhaust the sum rule and the error increases not only rapidly with N , but also with the strength of the core-hole potential. We have, however, found numerically that, for N ca. 80, no more than 4% of the total intensity is contributed by double-pair and higher excitations, even for very strong potentials that almost result in a bound state.

Having discussed the determinantal approach, we will now concentrate on the equivalent approach originally presented by Nozières and DeDominicis¹². This method leads to an integral equation whose solution in turn determines the x-ray spectrum. The solution is, however, rather difficult to obtain for ordinary local core-hole potentials, a disadvantage not encountered in the determinantal approach. One of the clear advantages of the integral-equation formulation lies in the fact that the equation can be solved asymptotically to yield the singular behavior of the spectra close to threshold¹². The main reason why we have chosen to base most of our work on this approach is, however, that it can rather easily be generalized to include the interaction between the electrons, thus eventually enabling us to go beyond ND theory. Such a generalization is very difficult to attain in the determinantal approach.

The starting expression is the same as for the determinantal approach, Eq. (2.7). The first step is to convert the δ -function into an integral in time-space giving

$$J(\omega) = \frac{1}{\pi} \operatorname{Re} \sum_s \int_{-\infty}^0 dt e^{it(\omega + \omega_s - \epsilon_F)} \cdot \langle N \sim | b^+ | N-1, s \rangle \langle N-1, s | b | N \sim \rangle \quad (2.17)$$

Then, from the definition of ω_s ($\omega_s = E_s(N-1) - E_0(N-1) = E_s(N-1) - \tilde{E}_0(N) + \tilde{E}_0(N) - E_0(N) + E_0(N) - E_0(N-1) = E_s(N-1) - \tilde{E}_0(N) - \Delta + \epsilon_F$) and from the completeness of the eigenstates $|N-1, s\rangle$ of H we obtain

$$J(\omega) = \frac{1}{\pi} \operatorname{Re} \int_{-\infty}^0 dt e^{it(\omega-\Delta)} \langle N \sim | b^\dagger e^{itH} b e^{-it\tilde{H}} | N \sim \rangle \quad (2.18)$$

Expanding b , for later convenience in the basis that diagonalizes $\tilde{H}$, the spectrum is finally given by

$$J(\omega) = \frac{1}{\pi} \operatorname{Re} \sum_{k,k'} \tilde{p}_{ck} \tilde{p}_{ck'}^* \int_{-\infty}^0 dt e^{it(\omega-\Delta)} \tilde{F}_{kk'}(t) \quad (2.19)$$

provided we know the correlation function

$$\tilde{F}_{kk'}(t) = \langle N \sim | \tilde{a}_{k'}^\dagger e^{iHt} \tilde{a}_k e^{-i\tilde{H}t} | N \sim \rangle \quad (2.20)$$

In Appendix 1 we show that $\tilde{F}_{kk'}(t)$ is a product of two quantities $\tilde{G}_{kk'}(t,t)$ and $\tilde{g}(t)$,

$$\tilde{F}_{kk'}(t) = -i \tilde{g}(t) \tilde{G}_{kk'}(t;t) \quad (2.21)$$

and that $\tilde{G}_{kk'}(\tau,t)$ can be obtained from the integral equation

$$\begin{aligned} \tilde{G}_{kk'}(\tau;t) &= \tilde{G}_k^0(\tau) \cdot \delta_{kk'} \\ &+ \sum_q \int_0^t \tilde{G}_k^0(\tau-\tau') \tilde{V}_{kq} \tilde{G}_{qk'}(\tau';t) d\tau' \end{aligned} \quad (2.22)$$

involving a free particle Green's function

$$G_k^0(\tau) = -i e^{-i\varepsilon_k \tau} \{ (1-n_k) \theta(\tau) - n_k \theta(-\tau) \} \quad (2.23)$$

which is diagonal in the H basis. Here, $\theta(\tau)$ is the usual Heaviside step function and the Fermi factor n_k is one or zero depending on whether the state k is occupied or not. The integral equation completely determines $\tilde{G}_{kk'}(\tau, t)$ in the interval $t \leq \tau \leq 0$ and in Appendix 1 we also show that $\tilde{g}(t)$ can be obtained from $\tilde{G}_{kk'}$ according to

$$\tilde{g}(t) = \exp \left\{ \sum_{k, k'} \int_t^0 \tilde{V}_{kk'} \tilde{G}_{kk'}(0; \tau) d\tau \right\} \quad (2.24)$$

Thus, in order to compute the emission spectrum we must first solve the integral equation (2.22) for a given core-hole potential, then obtain $\tilde{g}(t)$ from Eq. (2.24) and $\tilde{F}_{kk'}(t)$ from Eq. (2.21), and finally we must evaluate the Fourier transform and perform the sums prescribed by Eq. (2.19). The principal difficulty of this procedure lies in obtaining a solution to Eq. (2.22). For real solids, the label k is three-dimensional and we have an integral equation in four variables. Assuming a local spherical core-hole potential the equation can in many cases be reduced to a set of coupled integral equations in two variables but the solution to this simpler problem still requires a considerable effort. However, using a separable potential of the form

$$\tilde{V}_{kk'} = V_0 \tilde{p}_{ck}^* \tilde{p}_{ck'} \quad (2.25)$$

reduces the calculation of the spectrum to a truly one-dimensional problem in time-space. In writing the core-hole potential as in Eq. (2.25) we have actually

introduced two approximations, i) the potential is separable and ii) the k -dependence is governed by that of the dipole matrix element. It might appear as if the second approximation imposes too severe a restriction on the potential by leaving only one free parameter, V_0 , in order to model a realistic core-hole potential. It is, however, seen from Eq. (2.20) that $\tilde{F}_{kk'}(t)$ is nonzero only if both k and k' label occupied states and, therefore, by virtue of Eq. (2.19), we need the dipole matrix element $\tilde{p}_{ck}$ only below the Fermi level in order to obtain the spectrum. Consequently, we are free to choose $\tilde{p}_{ck}$ above the Fermi level at will and, in the present paper, we will show that this additional freedom suffices to allow us to model any local potential pertinent to a simple metal by means of the ansatz (2.25). We will use the determinantal approach, in which a local potential is no more difficult to treat than a separable potential, to show that, given a local potential we can find a separable model potential (Eq. (2.25)), which is equivalent to the former in the sense that both potentials give rise to almost the same dynamical spectrum.

We now demonstrate that, with the ansatz (2.25), our problem becomes essentially one-dimensional and comparatively simple. We define the auxiliary quantity

$$\tilde{G}(\tau, t) = \sum_{k, k'} \tilde{p}_{ck} \tilde{G}_{kk'}(\tau; t) \tilde{p}_{ck'}^* \quad (2.26)$$

in terms of which the spectrum is given by (Eqs. (2.19) and (2.21))

$$J(\omega) = \frac{1}{\pi} \operatorname{Im} \int_{-\infty}^0 e^{it(\omega-\Delta)} \tilde{g}(t) \tilde{G}(t;t) dt \quad (2.27)$$

Similarly we define the Green's function

$$\tilde{G}^0(\tau) = \sum_k \tilde{p}_{ck} G_k^0(\tau) \tilde{p}_{ck}^* \quad (2.28)$$

If we now multiply the integral equation (2.22) from the left by $\tilde{p}_{ck}$ and from the right by $\tilde{p}_{ck'}^*$, and sum over k and k' , these definitions and the ansatz (2.25) lead to the one-dimensional integral equation

$$\tilde{G}(\tau;t) = \tilde{G}^0(\tau) + V_0 \int_0^t \tilde{G}^0(\tau-\tau') \tilde{G}(\tau';t) d\tau' \quad (2.29)$$

and Eq. (2.24) becomes

$$\tilde{g}(t) = \exp \left\{ V_0 \int_t^0 \tilde{G}(0;\tau) d\tau \right\} \quad (2.30)$$

In terms of the density of states $\mathcal{D}(\epsilon)$, we also define the transition density of states (TDOS) obtained in the presence of the core-hole potential, $\tilde{A}(\omega)$, and the TDOS for the ground state solid with a filled core level, $A(\omega)$, by

$$\tilde{A}(\omega) = \left[\mathcal{D}(\varepsilon_k) |\tilde{p}_{ck}|^2 \right]_{\varepsilon_k = \omega} \quad (2.31)$$

$$A(\omega) = \left[\mathcal{D}(\varepsilon_k) |p_{ck}|^2 \right]_{\varepsilon_k = \omega} \quad (2.32)$$

Then the static initial and final state spectra defined by Eqs. (2.15) and (2.16) are given by the occupied part of the TDOS obtained in the presence and in the absence of the core hole, respectively.

$$J_i(\omega) = \tilde{A}(\omega) \theta(\varepsilon_F - \omega) \quad (2.33)$$

$$J_f(\omega) = A(\omega) \theta(\varepsilon_F - \omega) \quad (2.34)$$

With these definitions we find that the Green's functions $\tilde{G}^0(\tau)$ of Eq. (2.28) is completely specified by the TDOS of the initial state with the core hole,

$$\begin{aligned} \tilde{G}^0(\tau) = & -i\theta(\tau) \int_{\varepsilon_F}^{\infty} \tilde{A}(\varepsilon) e^{-i\varepsilon\tau} d\varepsilon \\ & + i\theta(-\tau) \int_{-\infty}^{\varepsilon_F} \tilde{A}(\varepsilon) e^{-i\varepsilon\tau} d\varepsilon \end{aligned} \quad (2.35)$$

With the ansatz (2.25), $\tilde{A}(\omega)$ can, as shown in Appendix 2, be evaluated analytically to yield the result

$$\tilde{A}(\epsilon) = A(\epsilon) \left\{ \left[1 - V_0 \int \frac{A(\epsilon') d\epsilon'}{\epsilon - \epsilon'} \right]^2 + V_0^2 \pi^2 A^2(\epsilon) \right\}^{-1} \quad (2.36)$$

in terms of the TDOS $A(\omega)$ of the final state, i.e. the TDOS of the perfect solid. In Appendix 2 we also show that the Fermi-level phase shift δ_F of the separable potential (Eq. (2.25)) is given by

$$\sin \delta_F = - V_0 \pi \sqrt{A(\epsilon_F) \tilde{A}(\epsilon_F)} \quad (2.37)$$

From the equations (2.36), (2.35), (2.29), (2.30), and (2.27) we see that the dynamical emission spectrum is completely determined by the TDOS $A(\omega)$ of the final state and the potential parameter V_0 . All results from the integral-equation approach presented in this work were obtained from these equations.

We will now describe the procedure used in our practical applications. In order to obtain the dynamical emission spectrum for a real solid, i.e. the spectrum predicted by ND theory, we first compute the static final-state spectrum for the solid, i.e. the spectrum obtained from one-particle theory in which the valence Bloch functions are used to calculate the transition matrix elements. Due to dipole selection rules, this spectrum has in general two angular momentum components. For instance, in the case of a core hole of p character, there is an s- and a d-contribution to the spectrum. We will consider

these contributions separately, one at a time. Such a procedure is based on the assumption that the full ND integral equation (2.22) is to a good approximation equivalent to a set of decoupled integral equations, one for each angular momentum channel. It is not difficult to show that this really is the case in a simple metal with cubic symmetry, assuming a spherical core-hole potential and neglecting $l=4$ and higher angular momentum components of the Green's function in the central cell. An ansatz of the form given by Eq. (2.25) can then be made for each angular momentum channel. For each channel we identify $A(\omega)$ below the Fermi level, i.e. the static final-state spectrum, with the transition density of states of the real system. From self-consistent impurity calculations for the real system with a core hole on one site, we next obtain the screened core hole potential, the corresponding Fermi-level phase shifts, and the angular-momentum decomposed transition density of states in the presence of the core hole⁶. For each channel we then determine V_0 and $A(\omega)$ above the Fermi level by the requirement that the phase shift given by Eq. (2.37) be the same as the true Fermi-level phase shift and that $\tilde{A}(\omega)$ from Eq. (2.36) be an optimal fit to the occupied part of the TDOS of the real system in the presence of the core hole. Due to the severe restrictions imposed by our separable ansatz (Eq. (2.25)), the fitted TDOS, i.e. the fitted initial state spectrum, may deviate considerably from the full result. A typical example is provided in Figure 2, where the full result is represented by the TDOS of a free-electron gas in the presence of a spherical square-well potential.

Owing to the sum rule given by Eq. (2.14), the weight of the dynamical spectrum, i.e. the integrated intensity below the Fermi level, is given by the weight of the static initial state spectrum and, therefore, it is essential to ensure that at any rate the weight of the fitted spectrum $\tilde{A}(\omega)$ be equal to that of the static initial-state spectrum of the real solid.

Having obtained $\tilde{A}(\omega)$ and V_0 in this way, we compute the Green's function $\tilde{G}^0(\tau)$ from Eq. (2.35) and solve the integral equation (2.29). For moderately large times, this equation can be solved by straight-forward iteration, but for large t and strong potentials V_0 , the iteration converges rather slowly. Therefore, in practice, we used a technique based on Pade' approximants⁴⁴. A few further parameters enter into the numerical procedures. The density of states of a particular angular momentum decays rather slowly for large energies. The dipole matrix elements, however, tend to zero rather rapidly at larger energies and, consequently, so does $A(\omega)$ (Eq. (2.32)). Since our procedure allows us to choose $A(\omega)$ rather freely above the Fermi level, we have decided to make it vanish above some high energy ϵ_M , usually chosen to be ca. $4 \epsilon_F$. The inverse of the total energy range of $A(\omega)$ (and of $\tilde{A}(\omega)$, Eq. (2.36)) will set the time scale for fine-structure in the Green's function $\tilde{G}^0(\tau)$. Thus the time step Δt of Simpson's rule that we used to evaluate the integral in Eq. (2.29) had to be chosen to be $\sim 1/(4\epsilon_M)$. Having solved the integral equation up to a maximal time $|t_M|$, we have to perform a Fourier transform (Eq. (2.27))

to obtain the spectrum. As merely cutting this integral at t_M introduces artificial oscillations, one can choose to obtain a broadened spectrum by including a factor $\exp(-\alpha|t|)$ (Lorentzian) or $\exp(-\beta t^2)$ (Gaussian) in the integrand, with parameters α or β chosen such that the integrand essentially vanishes beyond $|t_M|$. But in order to obtain a better resolution and an accurate description of the sharp singular feature at the Fermi edge, we apply a fitting procedure that allows us to do the Fourier integral analytically for large times ($t \rightarrow -\infty$). For large times the two main quantities $\tilde{G}(0,t)$ and $\tilde{G}(t,t)$, which according to Eqs. (2.27) and (2.30) determine the SXE spectrum, are fitted to the analytical expressions

$$V_0 \tilde{G}(0;t) = \frac{\delta_0^2}{\pi^2} \frac{1}{t} - iD_0 + C_0 t^{-\beta} e^{i(\Omega_0 t + \phi_0)} \quad (2.38)$$

$$e^{i\varepsilon_F t} \tilde{G}(t;t) = D e^{i\delta_1} |t|^{(2\frac{\delta_2}{\pi} - 1)} + C t^{-\gamma} e^{i(\Omega t + \phi)} \quad (2.39)$$

The real fitting parameters $C_0, C, D_0, D, \Omega_0, \Omega, \phi_0, \phi, \beta, \gamma, \delta_0, \delta_1$, and δ_2 are chosen so as to yield the least square deviation between these expressions and the corresponding quantities obtained from the integral equation. The fitting is done over time intervals of the form $(\sim 2/3 t_M, t_M)$ and repeated for successively larger $|t_M|$ until the fitting parameters remain almost unchanged. In this way we obtain a nearly exact solution to the integral equation

valid for all negative times. The analytical expressions were certainly not chosen ad hoc. Clearly, the constant term in Eq. (2.38) determines the position of the x-ray threshold (Eqs. (2.27), (2.30)) and the fitting parameter D_0 should converge to Δ in order to fix the threshold at the Fermi level ϵ_F . The first term of Eq. (37) gives, after Fourier transformation, a contribution of the form $(\epsilon_F - \omega)^{1 - (\delta_0/\pi)^2}$ to the singular threshold behavior. Provided the fitting parameter δ_0 equals δ_F , i.e. the Fermi level phase shift of the core hole potential, this is the correct suppression of the x-ray edge due to the Anderson "orthogonality catastrophe" ³². Similarly, the first term of Eq. (2.39) yields, close to threshold, a factor $(\epsilon_F - \omega)^{2(\delta_2/\pi)}$, which is the correct excitonic enhancement of the edge ³¹, provided the parameter δ_2 also equals δ_F . Furthermore, it follows from the asymptotic version of ND theory ¹² that we should also obtain $\delta_1 = \delta_F$. The last terms in Eqs. (2.38) and (2.39) are meant to describe the oscillations in time produced by the non-analytic behavior of the TDOS at the bottom of the band. It is indicative of the internal consistency of the fitting procedure that the parameters obtained in an unrestricted fit did, within a few percent, fulfill the requirements discussed above. This result can also be viewed as a numerical verification of the asymptotic expressions derived by ND ¹².

3. Theory of XPS.

In this section we will merely summarize those details of the theory of x-ray photoemission⁴⁵ that would enable the reader to repeat the calculations leading to the results presented in Sec. 5. In the so-called sudden approximation, which will be used here and which leads to a description of XPS in terms of the one-core-hole Green's function, this theory is actually a simpler version of the theory of x-ray emission presented in Sec. 2. Therefore, we can rely heavily on the results obtained there. The starting point is the same, the Golden Rule

$$I(\omega) = \sum_f |\langle f | T | i \rangle|^2 \delta(v + E_i - E_f) \delta(\omega + \epsilon_F - \epsilon_k) \quad (3.1)$$

where we have inserted an extra δ -function to account for the fact that the photoemitted electrons are usually analyzed according to their energy relative to the Fermi-level, $\epsilon_k - \epsilon_F$. The energy v of the exciting photon is assumed to be very large, resulting in a high kinetic energy ($\sim \epsilon_k$) of the photoemitted electron which then can be treated approximately as a free electron. The initial and final states of the XPS experiment differ from those of SXE. The initial state $|i\rangle$ is the ground state of N valence electrons and an occupied core orbital, $c^+|N\rangle$, and its energy is $E_0(N) + \epsilon_c$, in the notation of Sec. 2. In the sudden approximation the final state is written as

$a_k^+ |N, s \sim \rangle$, representing an outgoing bare electron in a state k that does not interact with the excited state s of the N valence electrons which are left in the presence of a core hole. The final-state energy is $\tilde{E}_s(N) + \epsilon_k$. The part of the transition operator T which couples the initial state to the chosen final states is now the hermitian conjugate to Eq. (2.2)

$$T = \sum_k p_{ck}^* a_k^+ c \quad (3.2)$$

The matrix element $\langle f | T | i \rangle$ becomes $\sum_k p_{ck}^* \langle N, s \sim | a_k a_k^+ c c^+ | N \rangle$. By definition $c c^+ | N \rangle = | N \rangle$, and we can safely assume that there is a negligible content of one-particle states with the very high energy ϵ_k in the ground state $| N \rangle$. Thus

$$\langle f | T | i \rangle = p_{ck}^* \langle N, s \sim | N \rangle \quad (3.3)$$

and by rearranging the energies in the δ -functions and using our definitions from Sec. 2, $E_o(N) - \tilde{E}_s(N) + \epsilon_c - \epsilon_k = \Delta - \tilde{\omega}_s + \epsilon_c - \omega - \epsilon_F = E_c - \epsilon_F - \omega_s - \omega$, we obtain

$$I(\omega) = \sum_k \sum_s |p_{ck}|^2 |\langle N, s \sim | N \rangle|^2 \cdot \delta(\nu + E_c - \epsilon_F - \tilde{\omega}_s - \omega) \delta(\omega + \epsilon_F - \epsilon_k) \quad (3.4)$$

Introducing the density of states $\mathcal{D}(\epsilon)$ to convert the sum over the label k to an integral over energies, we have

$$I(\omega) = \mathcal{D}(\omega + \varepsilon_F) |p_{ck}|^2_{\varepsilon_k = \omega + \varepsilon_F} \cdot \sum_s |\langle N, s \sim | N \rangle|^2 \delta(\omega + \tilde{\omega}_s - \nu - E_c + \varepsilon_F) \quad (3.5)$$

which shows that the threshold of the XPS spectrum is again determined by the core-electron binding energy relative to the Fermi energy $\varepsilon_F - E_c$ as was the threshold of the SXE spectrum. At high energies ω , the TDOS-factor in front of the sum over excited states s varies slowly with energy and can be considered as a constant over the width of the XPS line. Since absolute intensities are not measured, this constant can be omitted together with other slowly varying factors that actually should have appeared in front of the Golden Rule expression. Being primarily interested in the shape of the XPS line and not in its position, we define our shifted and renormalized spectrum $A_c(\omega)$ to be

$$A_c(\omega) = \sum_s |\langle N | N, s \sim \rangle|^2 \delta(\omega + \tilde{\omega}_s) \quad (3.6)$$

Obviously, the threshold has been shifted from $\omega = \nu + E_c - \varepsilon_F$ to $\omega = 0$, i.e. $A_c(\omega) = 0$ for $\omega > 0$. Due to the completeness of the states $|N, s \sim\rangle$ ⁴⁶, the renormalized spectrum fulfills the convenient sum rule

$$\int_{-\infty}^0 A_c(\omega) d\omega = 1 \quad (3.7)$$

Comparing the Eqs. (2.7) and (3.6) we see that XPS from a theoretical point of view, is indeed a simpler version of SXE. The determinantal technique for XPS is almost identical to that of SXE. The determinants $b^+|N-1,s\rangle$ in SXE are replaced by determinants $|N,s\rangle$ in XPS, the single pair and higher order excitations, however, are now to be described in the core-hole basis $\{\tilde{a}_k, \tilde{\phi}_k(\underline{r})\}$ which, for absorption, again corresponds to the final state of the system. The excitation energies should also be obtained in the presence of the core hole, although the distinction between core-hole ($\tilde{\epsilon}_k$) and no-core-hole (ϵ_k) eigenvalues becomes irrelevant already at rather small N . Thus

$$\begin{aligned}
 A_c(\omega) = & |\langle N|N\rangle|^2 \delta(\omega) \\
 & + \sum_{\mu,k} |\langle N|\tilde{a}_\mu^+ \tilde{a}_k|N\rangle|^2 \delta(\omega + \tilde{\epsilon}_\mu - \tilde{\epsilon}_k) \\
 & + \sum_{\mu,\nu,k,\ell} |\langle N|\tilde{a}_\mu^+ \tilde{a}_\nu^+ \tilde{a}_k \tilde{a}_\ell|N\rangle|^2 \delta(\omega + \tilde{\epsilon}_\mu + \tilde{\epsilon}_\nu - \tilde{\epsilon}_k - \tilde{\epsilon}_\ell) \\
 & + \dots \dots \dots
 \end{aligned} \tag{3.8}$$

For systems, with of the order of 100 s-waves in a box we have found numerically that the contributions from double pair excitations (third line of Eq. (3.8)) are very small and that higher order excitations can be neglected. Only if a very high accuracy is required in connection with strong core-hole potentials may double excitations be of some importance. This is demonstrated in Table 1 which, for two spherical square-well potentials of different

strengths, shows how well the spectrum fulfills the sum rule (3.7) when no excitations, single excitations, and also double excitations are included.

The equivalent integral-equation approach to the XPS spectrum is obtained in a way similar to that leading to the SXE spectrum, namely by expressing the δ -function in Eq. (3.6) as an integral over time t giving

$$A_c(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^{\infty} dt e^{i\omega t} \sum_s e^{i\tilde{\omega}_s t} \langle N | N, s \rangle \langle N, s | N \rangle \quad (3.9)$$

From the definition in Sec. 2 we have $\tilde{\omega}_s = \tilde{E}_s(N) - \tilde{E}_0(N) = \Delta + \tilde{E}_s(N) - E_0(N)$ and using the completeness of the states $|N, s\rangle$ we have

$$A_c(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^{\infty} dt e^{it(\omega + \Delta)} g(t) \quad (3.10)$$

when we defined the function $g(t)$ by

$$g(t) = \langle N | e^{i\tilde{H}t} e^{-iHt} | N \rangle \quad (3.11)$$

This function is quite analogous to the function $\tilde{g}(t)$ defined for the case of x-ray emission in Appendix 1 (Eq. (A1.8)), and $g(t)$ has to be obtained from an integral equation similar to that determining $\tilde{g}(t)$ (Eqs. (2.22) and (2.24)). The derivation of this new equation differs only in minor details from the derivation of e.g. Eq. (2.22) and we will here give only the final results for the case

of the separable potential defined in Eq. (2.25)⁴⁷. We obtain the integral equation

$$G(\tau; t) = G^0(\tau) + V_0 \int_0^t G^0(\tau - \tau') G(\tau'; t) d\tau' \quad (3.12)$$

where $G^0(\tau)$ is the non-interacting Green's function in the absence of the core hole given by

$$G^0(\tau) = -i\theta(\tau) \int_{\epsilon_F}^{\infty} A(\epsilon) e^{-i\epsilon\tau} d\epsilon \\ + i\theta(-\tau) \int_{-\infty}^{\epsilon_F} A(\epsilon) e^{-i\epsilon\tau} d\epsilon \quad (3.13)$$

in terms of $A(\epsilon)$, the transition density of states in the absence of the core hole. This integral equation uniquely determines the quantity $G(\tau; t)$ in the interval $0 \leq \tau \leq t$ and the function $g(t)$ is then given by

$$g(t) = \exp \left\{ + itV_0 \int A(\epsilon) d\epsilon - V_0 \int_0^t G^*(0; \tau) d\tau \right\} \quad (3.14)$$

Thus, in order to compute an XPS spectrum of a real solid - or for that matter an absorption spectrum (see below) - we identify $\tilde{A}(\epsilon)$ above the Fermi level with the one-particle transition density of states of the solid in the presence of the core hole. We then obtain $A(\epsilon)$ from the inverse of Eq. (2.36) and chose V_0 such that the Fermi-level phase shift from Eq. (2.37) is equal to that of the full core-hole potential. As the next steps we vary $\tilde{A}(\epsilon)$ below the Fermi level to obtain a good fit above the Fermi

level between $A(\epsilon)$ and the one-particle transition density of states of the ground state solid. Finally we calculate the Green's function $G^0(\tau)$ from Eq. (3.13), solve the integral equation (3.12), and compute the function $g(t)$ from Eq. (3.14) and the XPS spectrum from Eq. (3.10). If there are several important angular momentum channels the resulting spectra of each channel must be convoluted to form the total XPS spectrum. In simple metals it is essential to include both the s and the p channels.¹⁴

The XPS experiment can be thought of as an absorption experiment carried out at high energies and, it is thus not surprising that the SXA spectrum $J_{\text{SXA}}(\omega)$ can also be obtained from the procedure described above. Choosing the threshold at $\omega = \epsilon_F$ it is given by (cf. Eq. (2.27))

$$J_{\text{SXA}}(\omega) = -\frac{1}{\pi} \text{Im} \int_0^{\infty} dt e^{it(\omega-\Delta)} g^*(t) G(t;t) \quad (3.15)$$

This equation has been used in Ref. 14 to demonstrate the accuracy of the Final State Rule for absorption in several model systems. In the present paper we will, however, not present any absorption results.

In the free electron approximation the XPS spectrum is simply a δ -function at the edge and in ND theory it becomes a rather narrow sharp peak which asymptotically approaches a power-law singularity at the edge. For very strong core-hole potentials there can be structure due to strong shake-up processes at energies $\sim \epsilon_F$ below the edge

but there will be no satellite structure due to plasmons since there is no valence-valence interaction in the ND model. For simple metals, however, most of the total intensity is concentrated close to the edge and consequently, it is quite difficult by just looking at $A_c(\omega)$ to determine the energy range in which the actual ND spectrum approximately follows a power-law. Therefore, we have here decided to show our results for $A_c(\omega)$ in a more illustrative way ⁴⁸, in which the deviation from the asymptotic line shape becomes more apparent. To this end we define the exponent function $\alpha(t)$ according to

$$\begin{aligned}\alpha(t) &= \frac{iV_0}{2\pi} G^*(0;t) + \frac{\beta}{2\pi} & t > 0 \\ \alpha(t) &= \alpha^*(-t) & t < 0\end{aligned}\tag{3.16}$$

where β is short for $\Delta + V_0 \int A(\varepsilon) d\varepsilon$. From the Eqs. (3.11) and (3.14) we see that the spectral function $A_c(\omega)$ can be written as

$$A_c(\omega) = \frac{1}{2\pi} \int dt e^{i\omega t} \exp \left\{ 2\pi i \int_0^t \alpha(\tau) d\tau \right\} \tag{3.17}$$

In analogy with Eq. (2.38) it can be shown ¹² that the function $V_0 G(0;t)$, for large t , behaves asymptotically as

$$V_0 G(0;t) = -i\beta + \frac{\alpha}{t} \tag{3.18}$$

where the asymmetry index α of one angular momentum and spin channel is given by

$$\alpha = \frac{\delta_F^2}{\pi^2} \quad (3.19)$$

in terms of the Fermi-level phase shift δ_F of that channel. Thus, for large t we have asymptotically $\alpha(t) = i\alpha/(2\pi t)$. At energies close to the edge i.e. for small frequencies in $A_c(\omega)$, the dominant contribution to the Fourier integral in Eq. (3.17) comes from large t and by introducing a cut-off T in the integration over τ and replacing $\alpha(t)$ with its asymptotic form, both integrals in Eq. (3.17) can actually be carried out analytically and to logarithmic accuracy we obtain

$$A_c(\omega) = C \cdot |\omega|^{\alpha-1} \quad (3.20)$$

This is the asymptotic line shape derived by Nozières and DeDominicis but the constant C involves the cut-off parameter T , $C = (1/\pi) \cos(\pi(1-\alpha)/2) \Gamma(1-\alpha) T^\alpha$, and can thus not be obtained from the asymptotic arguments presented above. Obviously, the exponent function $\alpha(t)$ decays fast enough to be Fourier transformed and we have

$$\alpha(\omega) = \frac{1}{\pi} \operatorname{Im} \int_0^\infty dt e^{-i\omega t} \{ v_0 G(0;t) + i\beta \} \quad (3.21)$$

If we multiply Eq. (3.17) by ω , integrate by parts and introduce the inverse of this Fourier transform we obtain the relation $\omega A_c(\omega) = -\int d\omega' \alpha(\omega') A_c(\omega - \omega')$. Since the spectral

function $A_c(\omega)$ vanishes above the edge, i.e. $A_c(\omega)=0$ for $\omega>0$ (Eq. (3.6)), it follows from this relation that the same must be true for the exponent function $\alpha(\omega)$, i.e. $\alpha(\omega)=0$ for $\omega>0$, and we obtain the integral equation⁴⁸

$$-\omega A_c(\omega) = \int_{\omega}^0 \alpha(\omega-\omega') A_c(\omega') d\omega' \quad (3.22)$$

for the spectral function $A_c(\omega)$. With no frequency dependence in the exponent function, i.e. with $\alpha(\omega)=\alpha(0)$, this integral equation would be solved by the asymptotic expression (3.20) and we have the important relation

$$\alpha(0) = \alpha \quad (3.23)$$

which explains the name "exponent function" for $\alpha(\omega)$. Furthermore, the frequency-dependent deviation of $\alpha(\omega)$ from its value at the edge measures the deviation of the spectral function from the asymptotic result. The usefulness of the exponent function $\alpha(\omega)$ stems from the fact that the asymmetry index α obtained by fitting an asymptotic line shape with a variable α to a full ND spectrum is approximately equal to the average of $\alpha(\omega)$ over the fitting region as will be discussed in Sec. 5.

In practice, we solve the integral equation (3.12) for $G(0,t)$ and obtain $\alpha(\omega)$ from Eq. (3.21). The XPS line shape is then to be obtained either from the integral equation (3.22) or directly from Eq. (3.10), the two methods being equally convenient.

We end this section by noting an interesting sum rule. Due to the sum rule (3.7) for the spectral function $A_c(\omega)$ we have from Eq. (3.22)

$$\int_{-\infty}^0 \omega A_c(\omega) d\omega = - \int_{-\infty}^0 \alpha(\omega) d\omega = - \Delta_r \quad (3.24)$$

The last equality follows from the following considerations. Obviously, $\alpha(\omega)$ integrated over all frequencies is just $2\pi\alpha(t=0)$, which according to the Eqs. (3.16), (3.12), and (3.13), is equal to

$$\beta - V_0 \int_{\epsilon_F}^{\infty} A(\epsilon) d\epsilon = \Delta + V_0 \int_{-\infty}^{\epsilon_F} A(\epsilon) d\epsilon = \Delta + \langle N | V | N \rangle = \Delta_r \quad (\text{Eq. 2.6}).$$

Thus, the center of gravity of $A_c(\omega)$ falls at Δ_r below the edge. Shifting the edge back to the excitation energy of the core hole, the sum rule (3.24) is just a restatement of the well known rule that the center of gravity of the excitation spectrum remains at the Hartree-Fock eigenvalue irrespective of the strength of the satellite structure. This rule is valid in ND theory as well as in the fully interacting case⁴⁹. Of course, in the latter case the relaxation shift in a simple metal will have large contributions from the plasmon satellites in $A_c(\omega)$. Since ND theory does not account for these effects the corresponding "relaxation" shift is not relevant to real systems (c.f. Ref. 43).

4. Results for SXE and the Final State Rule.

We start this section by establishing the usefulness of the determinantal finite-N approach. Consider for a moment the spectrum $J_1^{(N)}(\omega)$ obtained from this approach using N electrons in a box and including only single particle-hole pair excitations in the sum over final states prescribed by Eq. (2.7). This spectrum consists of discrete lines. However, as the number (N) of electrons is increased, $J_1^{(N)}(\omega)$ first approaches a continuous spectrum⁵¹ $J_1(\omega)$ but eventually the spectrum collapses due to Anderson's orthogonality catastrophe³²

$$\left(\lim_{N \rightarrow \infty} J_1^{(N)}(\omega) = 0\right).$$

The spectrum $J_2^{(N)}(\omega)$ obtained by also including double-pair excitations experiences a similar evolution with increasing N . It approaches a continuous spectrum $J_2(\omega)$, but, in this case, the final collapse occurs at a much larger N . Including several particle-hole pairs, N may be even larger before the integrated intensity of the corresponding spectrum tends to zero and the sequence $J_1(\omega)$, $J_2(\omega)$, ... converges towards the exact spectrum $J(\omega)$ of the infinite system. As a matter of fact, we have, in the present paper, considered already $J_1(\omega)$ to be an accurate approximation to $J(\omega)$ but due to the computational difficulties associated with the inclusion of higher order excitations, it is unfeasible to properly study the convergence properties of an asymptotic

expansion as that described above. Fortunately, we are in a position to compare the approximate spectrum $J_1(\omega)$ directly with the result for the infinite system. Whereas the integral-equation approach in the simple version discussed here is limited to separable core-hole potentials, there is no restriction on the potential in the determinantal finite-N approach. In particular, we can compare results of the two methods using the same separable potential. Fig. 1 shows such a comparison in the case of a separable core-hole potential of the form given by Eq. (2.25) with dipole-matrix elements chosen to be

$$p_{ck} = \int e^{-\lambda r} \psi_k(r) d^3r \quad (4.1)$$

The final-state wave functions $\{\psi_k\}$ are taken to be free spherical waves. In all emission examples presented here we have had in mind $L_{2,3}$ emission spectra which are determined essentially by the TDOS of s character. The core hole then has p symmetry but, in a picture based on orthogonalized plane waves, the energy dependence of the transition matrix element p_{ck} is, at small energies, mainly determined by the direct overlaps between plane waves and the lower lying core states of s symmetry - in this case chosen to be a single 1s-function with a reciprocal radius λ of 1.25 inverse Bohr radii. Thus, the choice given by Eq. (4.1) has the correct energy dependence at smaller energies. The potential parameter V_0 is -2.24 Ry giving a Fermi-level phase shift $\delta_F = 0.90$. This phase shift as well as the density ($r_s = 4$) of the free

electron gas used to simulate the ground state solid both correspond approximately to sodium metal⁵². The spectrum from the finite-N approach is constructed using 80 s-waves in a spherical box and the possible final states are limited to those having only a single excited particle-hole pair. The close agreement between this spectrum and that obtained for the infinite solid using the integral-equation approach is strong evidence for the rapid convergence of the asymptotic expansion discussed above. This comparison has also been performed in other cases corresponding to different choices of parameters and with the same encouraging results. Thus, Fig. 1 should be considered as a typical case and the present investigation represents the first strict demonstration of the usefulness of the finite-N approach.

Next, we intend to establish that the use of a separable potential does not give rise to any spurious results. As a matter of fact, a separable potential and a local potential, i.e. a potential depending only on position, give rise to very much the same dynamical ND spectra provided the parameters of the separable potential are chosen such that the Fermi-level phase shift and the integrated intensity of the resulting static initial-state spectrum are the same as for the local potential. This important fact, which is exemplified in Fig. 2, renders the simple one-dimensional version of the integral-equation approach quite useful for the calculation of dynamical ND spectra of real solids. The curve labeled f is the static final-state spectrum (Eq. (2.16)), i.e. the

usual one-particle result with dipole matrix elements given by Eq. (4.1) in terms of free spherical waves. The curve marked $i_{sq.w.}$ is the static initial-state spectrum (Eq. (2.15) for which the dipole matrix elements have again been obtained from Eq. (4.1) but this time using free spherical waves perturbed by a spherical square-well potential of radius $r_c = 1.52$ Bohr radii and depth $V = -0.873$ Ry. The curve labeled $i_{sep.}$ is the static initial-state spectrum given by a separable potential determined as described at length in Sec. 2 (essentially from Eqs. (2.33), (2.34), (2.36), and (2.37)). In particular, this potential gives the same Fermi-level phase shift $\delta_F = 0.90$ as the square-well potential and the area under the two curves labeled $i_{sep.}$ and $i_{sq.w.}$ is the same. The curve labeled d is the dynamical ND result obtained from the finite- N approach ($N=80$) using either of the two potentials. Therefore, this curve actually consists of two curves separated by less than 1%, which demonstrates the effective equivalence of the two potentials. We stress again that the results presented in the figures should be considered as typical and not merely as a consequence of fortuitous circumstances. Note that the area under the dynamical curve is almost the same as under the two initial-state curves, the difference being due to the neglect of double-pair and higher order excitations. This is a consequence of the sum rule Eq. (2.14) and explains why the separable potential was chosen so as to give the same integrated initial-state intensity as the square-well potential. As seen in Fig. 2 the difference in shape of the two initial-state spectra has, however, no effect on

the resulting dynamical spectra which is a consequence of the Final State Rule according to which these spectra reflect the spectral properties of the final state.

The accuracy of the Final State Rule is the topic of the Figs. 3 - 9. According to this rule the dynamical ND spectrum $J(\omega)$ is well approximated by the formula

$$J(\omega) = C \cdot J_f(\omega) \left[\frac{\epsilon_F}{\epsilon_F - \omega} \right]^{2\frac{\delta_F}{\pi} - \frac{\delta_F^2}{\pi^2}} \quad (4.2)$$

where $J_f(\omega)$ is the static final-state spectrum given by Eq. (2.16) and C is a constant which is determined by the sum rule (2.14) stating the equality of the integrated intensities of the dynamical and the static initial-state spectra. An approximate derivation of Eq. (4.2) is given in Sec. 6. The importance of the Final State Rule derives from the fact that the rule a posteriori provides a justification for the numerous previous calculations of x-ray emission spectra based on band theory. The rule also shows how realistic x-ray emission and absorption spectra¹⁴ may be obtained from simple one-particle theory without resorting to complicated dynamical calculations for realistic systems. Finally, the rule exactly corresponds to the commonly used procedure for obtaining threshold exponents from experimental spectra. This procedure is thus justified by the high accuracy of the Final State Rule close to threshold. In Fig. 3 the spectrum from the Final State Rule is compared to the full

dynamic ND result chosen to be the same as in Figs. 1 and 2. In order to show the maximum deviation between the two spectra the constant C has here been chosen such that they agree at the Fermi level. Clearly the deviation at the bottom of the band is smaller than what can possibly be detected experimentally. It should be noted that the emission spectrum presented in Fig. 3 is representative of an emission spectrum in a simple metal, the Fermi energy and the corresponding phase shift approximating those found in sodium⁵².

The only parameters in Eq. (4.2) which depend on the core-hole potential are the constant C and the Fermi-level phase shift δ_F . Therefore, the Final State Rule implies that all core-hole potentials with the same phase shift will give rise to dynamical ND spectra of approximately the same shape. This prediction is tested in Fig. 4 showing ND spectra produced by three different square-well potentials with a common Fermi-level phase shift ($\delta_F = 0.90$). The final-state spectrum, labeled f , is the same in all three cases and also the same as in Figs. 1, 2, and 3. The static initial-state spectra indicated by the corresponding radii of the square wells are, however, quite different. Still, the resulting dynamical spectra are almost identical in shape. The weights of the initial-state spectra, i.e. their integrated intensities, differ by $\sim 10\%$. The dynamical spectra, here obtained from the finite- N approach ($N=80$), were, however, scaled to the same weight in order to facilitate the comparison of their shapes.

In order to demonstrate the usefulness of the Final State Rule also for very strong core-hole potentials we show in Fig. 5 dynamical ND spectra from the integral-equation approach using a separable core-hole potential which is strong enough to pull a bound state out of the band. The position of the bound state is indicated by the vertical arrow in the static initial-state spectrum (dashed-dotted curve) which is chosen to be the same for all three cases shown. We have instead decided to vary the static final-state spectrum (dashed curves) by leaving an attractive impurity potential of variable strength in the final state of the emission process. The Fermi-level phase shifts of the residual impurity potentials in the three cases are 0.64, 0.33, and 0.00 and thus the first two cases correspond to emission from an impurity site in a simple metal. As a matter of fact, the parameters of the transition density of states are chosen such that the first case ($\delta_F = 0.64$) simulates $L_{2,3}$ satellite emission in sodium. The initial state of this process has two core holes with a potential which causes a bound 3s-state to drop out of the band⁶. The final state has only one core hole but the corresponding potential is still strong enough to cause a large build-up of oscillator strength of s character towards the bottom of the band. As shown by Fig. 5 there remains no trace of the bound state in any of the dynamical spectra (full curves) which rather closely resemble their respective final-state spectra (dashed curves), the difference being due to the threshold singularities and the shake-up structure below the band in the dynamical spectra. Fig. 5 also demonstrates how the

strengths of the singularity and the shake-up structure vary with the strength of the core-hole potential. As shown in Ref. 52 the Fermi-level phase shift of the core-hole potential is given by the difference between the phase-shifts of the initial- and the final-state potentials. For the initial state we here have $\delta_F=1.01$ which in our three cases results in core-hole potentials having $\delta_F=0.37$, 0.68 , and 1.01 with smaller phase shifts and thus weaker singularities and weaker shake-up structure being associated with more attractive final-state potentials. The Final State Rule was challenged by Swarts, Dow, and Flynn in a rather recent Physical Review Letter²⁸. On the basis of the finite-N approach these authors presented numerical evaluations of the ND theory of emission and absorption spectra and they concluded that the spectra rather reflected the spectral properties of the initial state - at least for weaker core-hole potentials. For stronger potentials they claimed that the dynamical spectra could not be described by either of the two static limits. These conclusions are of course at odds with everything said so far in the present work. In order to resolve this controversy we have here repeated some of their calculations of emission spectra which were obtained by using a square-well core-hole potential in the free electron gas. The results are shown in the Figs. 6, 7, and 8 where, as before, i, f, and d label the static initial- and final-state spectra and the dynamical ND spectrum, respectively. Following Swarts et al. we have here used the valence wave function at the origin as a measure of the core-valence dipole matrix element. This is the reason

for the unphysically large ratio between the weights of the static initial- and final-state spectra. Above the spectra these figures also show an energy dependent function $C(\omega)$ which is defined according to

$$C(\omega) = \frac{J(\omega)}{J_f(\omega)} \left[\frac{\epsilon_F - \omega}{\epsilon_F} \right]^{2\frac{\delta_F}{\pi} - \frac{\delta_F}{\pi^2}} \quad (4.3)$$

Thus, an energy independent $C(\omega)$ leads directly to Eq. (4.2) and the deviation of $C(\omega)$ from a horizontal line measures the deviation from the Final State Rule. The very weak energy dependence that we find for $C(\omega)$ is strong evidence for the numerical accuracy of this rule. Only the strongest potential in Fig. 8 gave a minor deviation of the order of 10%⁵³, and this potential is more attractive than those found in real simple metals. Note that $C(\omega)$ rapidly tends to infinity very close to the bottom of the band. This does not signal a deviation from the Final State Rule but is merely a manifestation of the simple fact that the final-state spectrum vanishes at the band bottom whereas the dynamical spectrum, due to shake-up processes, is very small but finite. Thus, the results of Swarts, Dow, and Flynn accurately obey the Final State Rule and their erroneous conclusions most likely result from the misleading way in which they present their data.

In Fig. 9 we present a realistic $L_{2,3}$ emission spectrum of sodium obtained from the integral-equation approach. As described at length in Sec. 2 the s and p

angular momentum channels of the static initial- and final-state spectra were fitted to the corresponding channels of the one-particle spectra obtained from fully self-consistent calculations for sodium with and without a core hole on one site⁶. The very small d contribution to the spectrum was here neglected⁶. The resulting Fermi-level phase shifts of s and p character (0.58 and 0.33) are somewhat different from those generally expected on the basis of theory⁵² and XPS experiments³⁶. They rather correspond to those e.g. used by Calcott et al. in order to interpret their SXA experiment on sodium¹⁵. The resulting threshold exponent ($\alpha_0 = 0.23$) is intermediate between that used by Citrin⁵ ($\alpha_0 = 0.38$) to fit the absorption data of Kunz⁵⁴ and that used by Calcott et al.¹⁵ ($\alpha_0 = 0.15$) to fit their emission data. This ambiguity in the experimentally determined threshold exponents indicates that the physics of the x-ray edges is not yet fully understood. In particular, there is a need for further investigations of exchange effects and of the effects of valence-valence interactions not accounted for in the ND theory. Due to dipole selection rules only s electrons contribute to the static initial (i) and final (f) state spectra when d electrons are neglected. As seen in Fig. 9 the final-state spectrum (f) has a very smooth structureless appearance reflecting the almost parabolic s band of sodium whereas the initial-state spectrum (i) shows a strong s-resonance towards the bottom of the band due to the presence of the core hole. There is, however, no trace of this marked structure in the resulting dynamical ND spectrum whose shape rather resembles that of

the final-state spectrum only multiplied by a threshold singularity. This is demonstrated in detail by the insert showing the energy variation needed in the "constant" C in order to make Eq. (4.2) an exact relation. Thus, the deviation from the Final State Rule is only 10 % over half the band width, again demonstrating the numerical accuracy of the Final State Rule. Note that a slightly slanting $C(\omega)$ will not affect the interpretation of experimental spectra in terms of the Final State Rule since such an effect will probably be washed out by the background subtraction from the raw data. The curves labeled d_1 and d_2 in Fig. 9 explain why it is necessary to calculate also the p contribution to the transition density of states (TDOS). Whereas the initial- and final-state spectra and also the so called transient Green's function $G(t;t)$ (cf. Eqs. (2.22) and (2.26)) are entirely determined by the TDOS of s character, the dynamical spectrum has contributions from all angular momentum and spin channels via the "overlap" function $g(t)$ (Eq. (2.24). This is due to the fact that the sum in Eq. (2.24) must be carried out over all quantum labels including magnetic and spin quantum numbers. The additional channels cause a reduction of the threshold exponent and of the threshold singularity. For instance $2(\delta_F/\pi) - (\delta_F/\pi)^2$ in Eq. (4.2) becomes $2(\delta_o/\pi) - 2\sum_{\lambda} (2\lambda+1)(\delta_{\lambda}/\pi)^2$ in terms of the Fermi-level phase shifts δ_{λ} of the λ :th angular momentum channel¹². This effect is demonstrated in Fig. 9. The curve d_2 ⁵⁵ is the dynamical spectrum obtained without any orthogonality suppression of the threshold i.e. using $g(t) = 1$ in Eq. (2.27). The threshold exponent of this spectrum

is $2\delta_0/\pi$. The curve d_1 is the dynamical spectrum obtained by including both spin channels of s symmetry giving a threshold exponent $2(\delta_0/\pi) - 2(\delta_0/\pi)^2$. The curve d finally is the full dynamical spectrum obtained by also including all the p channels and the corresponding threshold exponent is $2\delta_0/\pi - 2(\delta_0/\pi)^2 - 6(\delta_1/\pi)^2$ ($\delta_\lambda \approx 0$, $\lambda \geq 2$). Fig. 9 demonstrates that it is essential to include the higher angular momentum channels in order to reduce the threshold singularity before a quantitative comparison with experiment is made.

5. Results for XPS.

The examination of the energy range over which the asymptotic power-law line shape of XPS is a close approximation to the full result of ND theory is, as noted in Sec. 3, done best by inspecting the exponent function $\alpha(\omega)$ (Eq. 3.21). In this way one avoids the difficult task of directly comparing two singular functions. It also becomes redundant to accurately determine the normalization constant of the asymptotic theory (Eq. (3.20)) which depends on the potential in a more complicated way than simply through the Fermi-level phase shift δ_F and whose uncertainty has plagued previous investigations³⁹. As described in Sec. 3, the determinantal approach leads immediately to the XPS spectrum (Eq. (3.8)), but in this approach $\alpha(\omega)$ can only be obtained indirectly from a somewhat inaccurate fitting procedure based on Eq. (3.22). In Fig. 10 we show $\alpha(\omega)$ for the case of $N=100$ free s-electrons in a box with a density corresponding to sodium ($r_s=4$) and a core-hole potential simulated by a square-well potential yielding a Fermi-level phase shift $\delta_F=1.3$. Note that the Fermi edge falls at $\omega=0$, i.e. to the left in Fig. 10. It is obvious from Eq. (3.22) that an $\alpha(\omega)$ which is constant over a certain range of energies away from the edge will yield a spectral function $A_c(\omega)$ which follows an exact power-law within this range. However, any structure in $\alpha(\omega)$ will yield a corresponding structure in $A_c(\omega)$. In Fig. 10 we

see that $\alpha(\omega)$ indeed remains rather constant over an appreciable fraction of the occupied band width. A fit to the corresponding spectral function over this range will disclose a very accurate power-law behavior. The obtained exponent will be some weighted mean of $\alpha(\omega)$ over this range and the variation of $\alpha(\omega)$ will set the error bar for the extracted exponent. For energies of the order of the Fermi energy ($\epsilon_F = 0.23$ Ry) away from the edge, one notes a broad peak (cf. e.g. Fig. 4.2) which is a consequence of the high probability for particle-hole excitations with an energy $\sim \epsilon_F$ due to the strong resonance at the bottom of the band (cf. e.g. Fig. 4.2), when it is calculated in the presence of the core hole. This structure has, however, only a minor effect on the spectral function, as the latter has become rather small this far from the edge. It should be noted that the phase shift of this system is larger than any value experimentally predicted or theoretically calculated for simple metals and would by itself almost exhaust Friedel's sum rule. In Fig. 11 we show exponent functions obtained from the integral-equation approach for a model system and five different separable core-hole potentials. The density of states was chosen to be a semi-elliptic band with ϵ_F at half the band width. The structure in $\alpha(\omega)$ at energies $\sim \epsilon_F$ away from the edge is here slightly sharper, reflecting the sharper peak in the density of states obtained in the presence of a separable core-hole potential (cf. e.g. Fig 4.2). The overall trend agrees with the result of Fig. 10, $\alpha(\omega)$ again being closely constant over about half the band width. Both a square-well and a separable potential thus

yield a similar behavior of $\alpha(\omega)$, and in a clear contradiction to what has been claimed by Dow et al.³⁹ we find the asymptotic power-law behavior to be valid over a substantial fraction of the band width away from the edge. We thus conclude that singularity indices may be rather accurately determined by fitting to experiment. Of course, cases may be constructed, either by distorting the density of states far from the free-electron behavior it has in simple metals or by applying excessively strong potentials, where the deviation of $\alpha(\omega)$ from a constant is strong already at small energies. But then we have left the physically reasonable world of simple metals.

Fig. 12 shows the exponent function $\alpha(\omega)$ for the system which we discussed at length in Sec. 4 in connection with Fig. 9 and which was chosen to closely model sodium. Also shown is the angular-momentum decomposition into the dominant s and p channels. While $\alpha(\omega)$ for both individual channels varies by almost 20% over half the bandwidth, the sum remains much more closely constant. In order to determine the effect of a varying $\alpha(\omega)$ on the commonly used procedure to determine the asymmetry index from the measured XPS line shape³⁶ we decided to consider the individual angular momentum and spin components of $\alpha(\omega)$ in sodium as representative of an energy dependent exponent function in a simple metal. The exact ND spectral function obtained by solving the integral equation (3.22) with $\alpha(\omega)$ given by one of these components, was broadened by a Gaussian and a Lorentzian with FWHM-values of 0.023 Ry and 0.003 Ry, respectively.

The Lorentzian width, reflecting the life time of the core hole, and the Gaussian width, reflecting phonon broadening, were chosen to values typical for XPS spectra of shallower core holes in simple metals³⁶. In an attempt to retrieve the input parameters the resulting spectrum was then fitted by a broadened version of the asymptotic form (Eq. (3.20)) by taking the two broadenings, the exponent, the threshold position, and the normalization as variational parameters. This defines the commonly used procedure for obtaining asymmetry indices from experimental spectra. The best fit was determined by minimizing the sum of the squared differences between the two spectra taken at equidistant points, 0.01 Ry apart, over varying fitting ranges. The result is given in Table II and shows the remarkable accuracy with which both the Lorentzian and the Gaussian broadenings could be determined. The accuracy of the exact threshold exponent is actually somewhat better than the accuracy claimed from experiment. We, thus conclude that even variations in the exponent function, $\alpha(\omega)$ which are stronger than those likely to be found in simple metals do not significantly affect the accuracy by which the asymmetry indices can be obtained from experiment. It should be remembered that this conclusion is based entirely on the ND theory which does not account for the interaction between the valence electrons. There is, however, yet no evidence indicating that the interaction effects might modify our conclusion. On the contrary, an investigation by Minnhagen³⁴ based on the theory of XPS derived by Langreth⁵⁶ indicates that the electron-electron interactions serve to make the XPS line shape more asymptotic.

6. Approximate derivation of the Final State Rule.

In this section we will present an approximate though rather accurate description of emission spectra from which the Final State Rule becomes rather evident. The discussion is based on the determinantal approach. In Secs. 2 and 3 we demonstrated that, in simple metals, this approach gives the correct answer to within $\sim 5\%$ already with rather small determinants ($N \sim 100$) and including only single pair excitations which are given by the first two lines of Eq. (2.12). In order to obtain an expression for the emission spectrum which can be evaluated analytically, we introduce the further approximation of restricting the electron of the excited electron-hole pair to be at the Fermi level. We then obtain

$$J(\omega) = \sum_k |\langle N \sim | b^+_{a_k} | N \rangle|^2 \delta(\omega - \epsilon_k) \quad (6.1)$$

Thus, this approximation simply corresponds to restricting the final states to be of the form $c^+_{a_k} | N \rangle$, i.e. Slater determinants consisting of one-particle orbitals evaluated in the final-state potential and having a single hole below the Fermi level. All shake-up processes are thus neglected.

In the case of a free electron gas with a core-hole potential approximated by a square-well potential with a Fermi-level phase shift δ_F equal to 1.1, we have found

numerically that this simple approximation gives an emission spectrum which is accurate to within 15% when $N=80$. This chosen potential is probably stronger than the actual core-hole potential of any simple metal and the approximation quickly improves as the Fermi-level phase shift is reduced. When $\delta_F=0.2\pi$ the error is only 6%. Since there are no shake-up processes, the approximation (6.1) can not account for the orthogonality suppression³² of the emission threshold and we thus expect Eq. (6.1) to give a spectrum with an exaggerated threshold singularity and too little intensity towards the bottom of the band. The main effect of the shake-up terms is, however, similar to a convolution with a power-law singularity. They are only important at threshold and Eq. (6.1) gives a sufficiently accurate description of the general shape of the emission band to allow us to demonstrate the Final State Rule in a qualitative way.

Inserting the expression (2.5) for the creation operator b^+ of the transition orbital into Eq.(6.1) we obtain

$$J(\omega) = \sum_k \left| \rho p_{ck} + \sum_{\mu} p_{c\mu} \beta_{\mu k} \right|^2 \delta(\omega - \epsilon_k) \quad (6.2)$$

in terms of the coefficients

$$\rho = \langle N | N \sim \rangle \quad (6.3)$$

$$\beta_{\mu k} = \langle N | a_k^+ a_{\mu} | N \sim \rangle \quad (6.4)$$

Note that greek and latin letters denote states above and below the Fermi level, respectively. Due to the completeness of the set of Slater determinants constructed from a complete set of one-particle states, the ground state $|N\sim\rangle$ obtained in the presence of the core hole can be expanded according to

$$\begin{aligned}
 |N\sim\rangle = & \rho |N\rangle + \sum_{\mu,k} \beta_{\mu k} a_{\mu}^+ a_k |N\rangle + \\
 & + \sum_{\mu,v,k,l} \gamma_{\mu v,k,l} a_{\mu}^+ a_v^+ a_k a_l |N\rangle + \dots \quad (6.5)
 \end{aligned}$$

Thus, the approximation (6.1) can alternatively be viewed as a truncation of this expansion after the term corresponding to single-pair excitations which should be an adequate procedure when the core-hole potential is not too strong. The overlap ρ is obviously equal to $\det S^{(N)}$ where $S^{(N)}$ is the overlap matrix involving only occupied state (cf. Eq. (A2.4))

$$S_{kk'}^{(N)} = \langle k | k' \sim \rangle, \quad \epsilon_k, \epsilon_{k'} \leq \epsilon_F \quad (6.6)$$

The coefficient $\beta_{\mu k}$, on the other hand, is the determinant obtained from $S^{(N)}$ by replacing the k :th row with the numbers $\langle \mu | k' \sim \rangle, \epsilon_{k'} \leq \epsilon_F$. Thus, expanding this determinant along the k :th row we obtain

$$\beta_{\mu k} = \det S^{(N)} \sum_{k'} \langle \mu | k' \sim \rangle S_{k'k}^{(N)-1} \quad (6.7)$$

in terms of the inverse $S^{(N)-1}$ of the overlap matrix $S^{(N)}$. At this stage we find it convenient to introduce a continuum approximation and convert discrete sums to integrals. For this purpose we rewrite Eq. (6.7) as

$$\sum_{k'} \beta_{\mu k'} S_{k'k} = \rho S_{\mu k} \quad (6.8)$$

and use the expression for $S_{kk'}$ derived in Appendix 2 (Eq. (A2.15))

$$\beta_{\mu k} + \frac{1}{\pi} \tan \delta_k \frac{p_{ck}}{A(\epsilon_k)} \sum_{k'} \frac{\beta_{\mu k'} p_{ck'}^*}{\epsilon_{k'} - \epsilon_k} = \rho \frac{1}{\pi} \tan \delta_k \frac{p_{ck}}{A(\epsilon_k)} \frac{p_{c\mu}^*}{\epsilon_{\mu} - \epsilon_k} \quad (6.9)$$

Defining the auxiliary quantity γ_k as

$$\gamma_k = \mathcal{D}(\epsilon_k) p_{ck}^* \sum_{\mu} p_{c\mu} \beta_{\mu k} \quad (6.10)$$

and converting sums over k and μ to integrals over the corresponding energy intervals, we obtain the following integral equation for $\gamma(\epsilon)$

$$\gamma(\epsilon) + \frac{1}{\pi} \tan \delta(\epsilon) \int_{-\infty}^{\epsilon_F} \frac{\gamma(\epsilon')}{\epsilon' - \epsilon} d\epsilon' = \frac{\rho}{\pi} \tan \delta(\epsilon) \int_{\epsilon_F}^{\infty} \frac{A(\epsilon')}{\epsilon' - \epsilon} d\epsilon' \quad (6.11)$$

Note that the overlap ρ tends to zero in the continuum limit $N \rightarrow \infty$. The decay is, however, governed by the formula

$$\rho = \rho_0 \cdot N^{-(\delta_F/\pi)^2/32}.$$

It is thus rather slow and ρ is still appreciable when the solution to the continuous integral equation (6.11) represents an accurate approximation to the discrete problem given by Eq. (6.7). As noted above, Eq. (6.2) yields a rather accurate spectrum with as many as 80 s-waves in a box and in this case the level spacing is small enough for the continuum approximation to be reliable. It should be remembered that this approximation is merely a convenient tool which permits us to penetrate the mechanisms leading to the results of the determinantal approach.

As demonstrated in Appendix 3, the seemingly complicated integral equation for $\gamma(\epsilon)$ can actually be solved analytically using a method due to Muskhelishvili⁵⁷ and the result is

$$\gamma(\epsilon) = \frac{\rho}{\pi} \frac{A(\epsilon)}{\eta(\epsilon)} \int_{\epsilon_F}^{\infty} \frac{\eta(\epsilon') \sin \delta(\epsilon')}{\epsilon' - \epsilon} d\epsilon' \quad (6.12)$$

in terms of the function

$$\eta(\epsilon) = \exp \left\{ \frac{1}{\pi} \int_{\epsilon_F}^{\infty} \frac{\delta(\epsilon')}{\epsilon - \epsilon'} d\epsilon' \right\} \quad (6.13)$$

Remembering that the final state spectrum $J_f(\omega)$ is just the occupied part of the TDOS $A(\omega)$ obtained in the absence of the core hole (Eq. (2.34)), we can combine the Eqs. (6.2), (6.10), (2.32), and (6.12) in order to express the

approximate dynamical ND spectrum $J(\omega)$ in terms of the static final state spectrum $J_f(\omega)$,

$$J(\omega) = \rho^2 J_f(\omega) \left[1 + \frac{1}{\pi \eta(\omega)} \int_{\varepsilon_F}^{\infty} \frac{\eta(\varepsilon) \sin \delta(\varepsilon)}{\varepsilon - \omega} d\varepsilon \right]^2 \quad (6.14)$$

In Fig. 13 we compare the spectrum obtained from a direct numerical evaluation of this formula and the spectrum obtained from the integral-equation approach with a separable potential having a phase shift $\delta_F=0.90$. The similar shapes of the two spectra suggest that our approximate treatment is sufficiently accurate to allow us to use it for a qualitative derivation of the Final State Rule. In order to study the behavior of the function $\eta(\varepsilon)$ we introduce an energy cut-off ε_0 in the integral in Eq. (6.13) and obtain

$$\eta(\varepsilon) = \left| \frac{\varepsilon - \varepsilon_F}{\varepsilon - \varepsilon_0} \right|^{\delta_F/\pi}, \quad |\varepsilon - \varepsilon_F| \rightarrow 0 \quad (6.15)$$

Thus, towards the Fermi level, the function $\eta(\varepsilon)$ tends to zero, whereas the inverse which appears in Eq. (6.14) has a power-law singularity with exponent δ_F/π . Directly from the defining equation we see that $\eta(\varepsilon)$ is everywhere positive and that it tends to unity at large energies. Towards the bottom of the band it tends to a constant of order $\exp(-2\delta_F/\pi) < 1$. From these properties and from the fact that the phase shift above ε_F usually is a slowly varying function which tends to zero as $\varepsilon^{-1/2}$ it follows that the integral in Eq. (6.14) gives rise to a monotonically increasing function which actually is small,

typically of the order of 0.1, at the bottom of the band and which reaches a value of the order of unity at the Fermi level. Consequently, the entire enhancement factor defined as the ratio of the dynamical spectrum and the final state spectrum, i.e. ρ^2 times the square in Eq. (6.14), has a smooth behavior, tending to a constant of order unity towards the bottom of the band and exhibiting a power-law singularity at the Fermi energy with a threshold exponent equal to $2\delta_F/\pi$. As a matter of fact, the enhancement factor is quite well represented by the simple

expression
$$C(\omega) \cdot \left[\frac{\epsilon_F}{\epsilon_F - \omega} \right]^{2\delta_F/\pi}$$

where the function $C(\omega)$ is almost constant over the entire occupied band. We thus have the approximate result

$$J(\omega) = C \cdot J_f(\omega) \left[\frac{\epsilon_F}{\epsilon_F - \omega} \right]^{2\delta_F/\pi} \quad (6.16)$$

in terms of a known but irrelevant constant C . This is the Final State Rule for emission disregarding shake-up effects. As mentioned previously, such effects are not included in the simple approximation given by Eq. (6.1) which, however, correctly describes the excitonic enhancement³¹ of the threshold as is evident from Eq. (6.16). In the time representation the shake-up effects enter (c.f. Eq. (2.21)) the ND theory via the multiplicative factor $g(t)$ given by Eq. (2.24). Therefore, these effects should really be accounted for via a convolution in frequency space. However, close to threshold the Fourier transform of $g(t)$ behaves as

$$(\epsilon_F - \omega)^{(\delta_F/\pi)^2 - 1}$$

describing the suppression of the edge due to the Andersson orthogonality catastrophe³². Thus, close to threshold the distinction between convoluting with this expression or multiplying by

$$(\epsilon_F - \omega)^{(\delta_F/\pi)^2}$$

becomes irrelevant and we have found numerically that over most of the occupied band the shake-up effects are well accounted for by merely changing the exponent in Eq. (6.16) to $2(\delta_F/\pi) - (\delta_F/\pi)^2$. Of course, at the very bottom of the band the final state spectrum vanishes whereas the dynamical spectrum is finite if shake-up effects are included. Therefore, the exact enhancement factor blows up close to the band bottom, a tendency which is apparent from the Figs. 6-9. Disregarding this minor effect the Final State Rule reads

$$J(\omega) = C \cdot J_f(\omega) \left[\frac{\epsilon_F}{\epsilon_F - \omega} \right]^{2\frac{\delta_F}{\pi} - \frac{\delta_F^2}{\pi^2}} \quad (4.2)$$

7. Conclusions.

The Final State Rule was established by the authors in 1977. The rule states that, disregarding the singular Fermi edges, accurate x-ray emission and absorption spectra of simple metals may be obtained from ordinary one-electron theory provided the relevant dipole matrix elements are calculated from valence wave functions obtained in the potential of the final state of the x-ray process i.e. a potential reflecting the fully screened core hole in absorption but not in emission. The Final State Rule also states that even the singular threshold behavior can be accurately accounted for via power-law factors with properly chosen exponents one for each angular momentum component of the spectrum. The importance of the Final State Rule stems from the fact that this rule a posteriori provides a justification for the numerous earlier calculations of x-ray emission spectra based on band theory. The rule also shows how to obtain realistic x-ray emission and absorption spectra without resorting to complicated many body calculations for real solids. Finally the rule corresponds exactly to the commonly used procedure for obtaining threshold exponents from measured x-ray spectra. Thus, the accuracy of the Final State Rule provides strong support for this procedure.

In the present paper we have made an extensive investigation of the validity of the Final State Rule.

This investigation is based entirely on the theory of x-ray spectra due to Nozières and DeDominicis¹². For numerous realistic model systems including cases where the core-hole potential is strong enough to pull a bound state out of the band we evaluate the ND theory numerically and show that the resulting dynamical ND emission spectra accurately obey the Final State Rule. In fact, to date, no case is known for which the ND spectrum does not follow the Final State Rule rather closely. In Sec. 6 we present an approximate version of the ND theory for emission spectra which can be evaluated analytically and which leads naturally to the Final State Rule. This approximate theory provides further support for the Final State Rule as applied to ND spectra and the theory also gives some insight into the mechanisms behind the rule. For the numerical evaluations of the ND theory we have used two different methods namely the integral-equation approach originally suggested by Nozieres and DeDominicis¹² and the determinantal finite-N approach first discussed by Friedel²⁹. The integral-equation approach pertains to an infinite system while the finite-N approach is based on a finite number (N) of electrons enclosed in a finite volume. In the limit of large N we show here both formally and numerically that the two methods are equivalent. In fact, by directly comparing the two methods we are able to prove that the finite N -approach gives rather accurate results already with an unexpectedly small number of particles ($N \sim 100$), thus rendering this approach quite useful for the calculation of x-ray and x-ray photoemission spectra. The approach based on the integral

equation is greatly facilitated by the use of a separable core-hole potential and in our applications we have always taken advantage of this possibility. By directly comparing to the finite-N approach which handles all potentials with equal ease we show here, that a separable potential does not give rise to any spurious results. In fact, we show that any square-well potential and probably also any reasonable local potential can be effectively simulated by a separable potential. If the parameters of the separable potential are chosen such that this potential and the square well yield the same Fermi-level phase shift and the same integrated intensity of the static spectrum obtained in the presence of the core hole, then the two potentials give rise to almost the same dynamical ND spectra. Thus, the approach based on the integral equation in connection with separable core-hole potential is also a very useful tool for obtaining x-ray spectra for realistic systems.

In the present work we also discuss at length the application of the ND theory to XPS. According to the asymptotic version of this theory the XPS line shape close to the edge obeys a power-law with an exponent determined by the asymmetry index. This fact forms the basis for the fitting procedure commonly used for extracting asymmetry indices from the measured XPS line shapes. The validity of this procedure thus relies on the validity of the asymptotic theory over the fitting range. We here analyze the full ND result for the XPS line shape in terms of the exponent function $\alpha(\omega)$ whose deviation from a constant measures the deviation of the asymptotic ND theory from

the full ND theory. This procedure avoids the difficulties associated with a direct comparison of two singular spectra as well as the ambiguous choice of normalization constant which has sometimes plagued other treatments³⁹. We here present results for the exponent function $\alpha(\omega)$ for several model systems which are chosen to correspond closely to real simple metals and we find that $\alpha(\omega)$ is indeed rather constant over about half the band width away from the edge. We also study the effect of a varying $\alpha(\omega)$ by applying the fitting procedure to broadened versions of XPS spectra obtained from exponent functions with a rather large variation with energy. The extracted asymmetry indices and broadenings were found to be very close to their exact values demonstrating the insensitivity of the extracted parameters to deviations from the asymptotic theory. These findings provide strong support for the accuracy of the commonly used fitting procedure.

Whereas the x-ray emission spectra of simple metals are dominated by electrons of a particular angular momentum symmetry the asymmetries of the XPS lines are strongly affected by particle-hole excitations of both s and p character. This is demonstrated here in the case of sodium by analyzing the exponent function $\alpha(\omega)$ into its angular momentum components. Since these particle-hole excitations act to reduce the threshold singularities of x-ray spectra we show here that it is essential to include this effect before a detailed comparison is made between dynamical ND spectra and experiment.

In several papers ^{28, 39, 41} Dow and co-workers have reached conclusions which are contradictory to most of the main results of the present paper. Their erroneous conclusions may be due to the misleading way in which they present their results and to their often unphysical choice of parameters.

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8. Appendix 1.

Following work by Langreth⁴², we will here give an elementary derivation of the basic integral equation of the original ND theory¹². We wish to compute the correlation function $\tilde{F}_{kk},(t)$ for negative times ($t < 0$). To this end we introduce a dummy variable τ into $\tilde{F}_{kk},$

$$\tilde{F}_{kk},(\tau;t) = \langle N\sim | \tilde{a}_k^+ e^{iH\tau} \tilde{a}_k e^{iH(t-\tau)} e^{-i\tilde{H}t} | N\sim \rangle \quad (A1.1)$$

in such a way that $\tilde{F}_{kk},(t) = \tilde{F}_{kk},(t;t)$, and take the derivative with respect to τ ,

$$i\partial_\tau \tilde{F}_{kk},(\tau;t) = \langle N\sim | \tilde{a}_k^+ e^{iH\tau} [\tilde{a}_k, H] e^{iH(t-\tau)} e^{-i\tilde{H}t} | N\sim \rangle \quad (A1.2)$$

The commutator is obtained from the expression for the no-hole Hamiltonian H in terms of the core-hole basis (Eq. (2.11))

$$[\tilde{a}_k, H] = \epsilon_k \tilde{a}_k - \sum_q \tilde{V}_{kq} \tilde{a}_q \quad (A1.3)$$

which leads to a closed equation for $\tilde{F}_{kk},(\tau;t)$

$$(i\partial_\tau - \epsilon_k) \tilde{F}_{kk},(\tau;t) = - \sum_q \tilde{V}_{kq} \tilde{F}_{qk},(\tau;t) \quad (A1.4)$$

It is not difficult to see that the free-particle Green's function defined in Eq. (2.23) is an ordinary Green's functions for this first order differential equation and we have

$$(i\partial_\tau - \epsilon_k) G_k^0(\tau) = \delta(\tau) \quad (A1.5)$$

After multiplying Eq. (A1.4) by $G_k^0(\tau' - \tau)$, integrating by parts and interchanging dummy variables τ and τ' , we obtain

$$\begin{aligned} \tilde{F}_{kk}(\tau; t) &= i\tilde{G}_k^0(\tau - t)\tilde{F}_{kk}(t; t) - i\tilde{G}_k^0(\tau)\tilde{F}_{kk}(0; t) + \\ &+ \sum_q \int_0^t d\tau' \tilde{G}_k^0(\tau - \tau') \tilde{V}_{kq} \tilde{F}_{qk}(\tau'; t) \end{aligned} \quad (A1.6)$$

Now, clearly from the definition, Eq. (2.20), the state k in $\tilde{F}_{kk}(t) = \tilde{F}_{kk}(t; t)$ must be occupied. We are, however, only interested in times $t \leq \tau \leq 0$ (Eq. (A1.6)). Therefore, from Eq. (2.23), $G_k^0(\tau - t) = 0$, and the first term of this equation vanishes. Since $\tau \leq 0$ the definition of $G_k^0(\tau)$ requires k to label an occupied state also in the second term of this equation which leads to

$$\begin{aligned} n_k \tilde{F}_{kk}(0; t) &= n_k \langle N \sim | \tilde{a}_k^+ a_k e^{iHt} e^{-i\tilde{H}t} | N \sim \rangle = \\ &= n_k \delta_{k, k'} \langle N \sim | e^{iHt} e^{-i\tilde{H}t} | N \sim \rangle \end{aligned} \quad (A1.7)$$

Consequently, the quantity $\tilde{g}(t)$ defined by

$$\tilde{g}(t) = \langle N\sim | e^{iHt} e^{-i\tilde{H}t} | N\sim \rangle \quad (A1.8)$$

must be a factor in $\tilde{F}_{kk'}(\tau, t)$ and by defining the auxiliary quantity

$$\tilde{G}_{kk'}(\tau; t) = i \tilde{F}_{kk'}(\tau; t) / \tilde{g}(t) \quad (A1.9)$$

we obtain the integral equation (2.22). This equation evidently determines $\tilde{G}_{kk'}(\tau, t)$ in the entire interval $t \leq \tau \leq 0$, but we still need $\tilde{g}(t)$ in order to find $\tilde{F}_{kk'}(t)$. From the Eqs. (A1.6), (2.10), and (2.11) we obtain

$$\begin{aligned} \sum_{k, k'} \tilde{V}_{kk'} \tilde{F}_{kk'}(\tau; t) &= \langle N\sim | V e^{iHt} e^{-i\tilde{H}t} | N\sim \rangle = \\ &= i \partial_t \langle N\sim | e^{iHt} e^{-i\tilde{H}t} | N\sim \rangle \end{aligned} \quad (A1.10)$$

where we have used the fact that $|N\sim\rangle$ is an eigenstate of $\tilde{H}$ to obtain the second equality. Thus

$$\tilde{g}(t) \sum_{k, k'} \tilde{V}_{k, k'} \tilde{G}_{kk'}(0, t) = - \partial_t \tilde{g}(t) \quad (A1.11)$$

and since $\tilde{g}(0) = 1$ (Eq. (A1.8)) this differential equation has the solution given by Eq. (2.24).

9. Appendix 2.

We will here show how the transition density of states (TDOS) in the presence of a core-hole is obtained from that of the ground state when the core-hole potential has the separable form given by Eq. (2.25). From the definitions of the TDOS's, Eqs. (2.31) and (2.32) we obviously need the dipole matrix elements $\tilde{p}_{ck}$ and p_{ck} with and without the core hole and the corresponding one-particle states $|k\sim\rangle$ and $|k\rangle$. These are eigenstates of the one-particle Hamiltonians $\tilde{H}$ and H defined by the Eqs. (2.8) and (2.9). Thus,

$$H |k\rangle = \epsilon_k |k\rangle \quad (A2.1)$$

$$\tilde{H} |k\sim\rangle = \tilde{\epsilon}_k |k\sim\rangle \quad (A2.2)$$

where the eigenvalues are assumed to be in the continuum. Since the perturbing potential $V = \tilde{H} - H$ has a finite range, the eigenvalues can also be assumed to be equal, $\tilde{\epsilon}_k = \epsilon_k$. The eigenstates of H form a complete set and we have

$$\tilde{p}_{ck} = \sum_{k'} p_{ck'} S_{k'k} \quad (A2.3)$$

in terms of the overlap matrix S defined by

$$S_{kk'} = \langle k | k'\sim \rangle \quad (A2.4)$$

The overlap matrix is easily obtained directly from the

eigenvalue equations (A2.1) and (A2.2)

$$S_{kk'} = \frac{\langle k | V | k' \sim \rangle}{\varepsilon_{k'} - \varepsilon_k} + d_k \delta_{kk'} \quad (\text{A2.5})$$

where the continuous nature of the eigenvalue spectrum has made it necessary to add a delta function with an unknown normalization constant d_k . Again using the completeness of the states $|k\rangle$, we can express the matrix element $\langle k | V | k' \sim \rangle$ in terms of the overlap matrix and by means of the separable ansatz (2.25) and Eq. (A2.3) we obtain $\langle k | V | k' \sim \rangle = V_0 p_{ck}^* p_{ck'}$. Thus,

$$S_{kk'} = V_0 \frac{p_{ck}^* \tilde{p}_{ck'}}{\varepsilon_{k'} - \varepsilon_k} + d_k \delta_{kk'} \quad (\text{A2.6})$$

Inserting this expression back into Eq. (A2.3) and using the density of states $\mathcal{D}(\varepsilon)$ to convert the sum over k to an energy integral, we obtain

$$\tilde{p}_{ck} = V_0 \tilde{p}_{ck} \int \frac{A(\varepsilon)}{\varepsilon_k - \varepsilon} d\varepsilon + d_k p_{ck} \quad (\text{A2.7})$$

We have here also used the definition, Eq. (2.32), of the TDOS in the absence of the core hole, $A(\varepsilon)$. Thus, it only remains to determine the normalization d_k , which we obtain from the orthonormality of the states $|k \sim \rangle$, i.e.

$$\delta_{kk'} = \langle k \sim | k' \sim \rangle = \sum_i S_{ik}^* S_{ik'} \quad (\text{A2.8})$$

Inserting the expression (A2.6) for the overlap matrix into this normalization condition leads to

$$\delta_{kk'} = v_o^2 \tilde{p}_{ck}^* \int \frac{A(\epsilon) d\epsilon}{(\epsilon_k - \epsilon)(\epsilon_{k'} - \epsilon)} \tilde{p}_{ck'} +$$

$$+ v_o d_k^* \frac{p_{ck}^* \tilde{p}_{ck'}}{\epsilon_{k'} - \epsilon_k} + v_o d_{k'} \frac{p_{ck'} \tilde{p}_{ck}^*}{\epsilon_k - \epsilon_{k'}} + |d_k|^2 \delta_{kk'} \quad (A2.9)$$

The integral on the first line of this expression obviously becomes singular when ϵ_k equals $\epsilon_{k'}$, and we can here use the well known mathematical identity

$$\int \frac{A(\epsilon) d\epsilon}{(\epsilon_k - \epsilon)(\epsilon_{k'} - \epsilon)} = \pi^2 A(\epsilon_k) \delta(\epsilon_k - \epsilon_{k'})$$

$$+ \frac{1}{\epsilon_{k'} - \epsilon_k} \left\{ \int \frac{A(\epsilon) d\epsilon}{\epsilon_k - \epsilon} - \int \frac{A(\epsilon) d\epsilon}{\epsilon_{k'} - \epsilon} \right\} \quad (A2.10)$$

The last two terms of this identity give rise to two terms which cancel the second and the third terms on the right hand side of Eq. (A2.9), and introducing the density of states factor $\mathcal{D}(\epsilon)$, the energy-delta function can be converted to a delta function in k and k' , $\delta(\epsilon_k - \epsilon_{k'}) = \mathcal{D}(\epsilon) \delta_{kk'}$. Finally, introducing the definition (2.31) of the TDOS in the presence of the core hole, $\tilde{A}(\epsilon)$, Eq. (A2.9) becomes

$$1 = v_o^2 \pi^2 \tilde{A}(\epsilon_k) A(\epsilon_k) + |d_k|^2 \quad (A2.11)$$

which determines the normalization d_k to within a phase factor of no relevance to the final result for $\tilde{A}(\epsilon)$. The phase factor can e.g. be chosen as $\exp(i\delta_k)$ where δ_k is

the phase shift. This choice can be seen to correspond to ordinary scattering theory or T-matrix theory whereas a choice of unity corresponds to scattering theory based on the reaction matrix⁵⁸. Preferring real quantities, we made the latter choice. Inserting the result given by Eq. (A2.11) into Eq. (A2.7), we obtain $\tilde{p}_{ck}$ and thus $\tilde{A}(\epsilon)$ from the definition (2.31). This leads to Eq. (2.36) of the main text.

Eq. (A2.11) allows us to write

$$\cos \delta_k = d_k \quad (A2.12)$$

$$\sin \delta_k = -\pi V_0 \{ A(\epsilon_k) \tilde{A}(\epsilon_k) \}^{1/2} \quad (A2.13)$$

in terms of an angle δ_k which obviously is positive for attractive potentials ($V_0 < 0$) and tends linearly to zero with the potential. It is not difficult to see that δ_k defined in this way corresponds to the usual definition of a scattering phase shift. The Eq. (2.36) then also gives the convenient relation

$$\tan \delta_k = -\pi V_0 A(\epsilon_k) \left\{ 1 - V_0 \int \frac{A(\epsilon) d\epsilon}{\epsilon_k - \epsilon} \right\}^{-1} \quad (A2.14)$$

Finally, from the Eqs. (A2.6), (A2.7), (A2.12), and (A2.14) we arrive at the following expression for the overlap matrix S

$$S_{kk'} = \frac{1}{\pi} \frac{p_{ck}^* p_{ck'}}{\epsilon_k - \epsilon_{k'}} \frac{\sin \delta_{k'}}{A(\epsilon_{k'})} + \cos \delta_{k'} \delta_{kk'} \quad (A2.15)$$

10. Appendix 3.

We will here use a method due to Muskhelishvili⁵⁷ to solve the integral equation (6.11). The Cauchy integrals

$$\Gamma(z) = \int_{-\infty}^{\varepsilon_F} \frac{d\varepsilon'}{2\pi i} \frac{\gamma(\varepsilon')}{\varepsilon' - z} - \rho \int_{\varepsilon_F}^{\infty} \frac{d\varepsilon'}{2\pi i} \frac{A(\varepsilon')}{\varepsilon' - z} \quad (\text{A3.1})$$

define two analytic functions, one in the upper half of the complex z -plane and one in the lower half. Denoting the limiting values of these functions on the real axis by $+$ and $-$ and concentrating on the part of the axis to the left of ε_F , we obtain

$$\Gamma^+(\varepsilon) = \int_{-\infty}^{\varepsilon_F} \frac{d\varepsilon'}{2\pi i} \frac{\gamma(\varepsilon')}{\varepsilon' - \varepsilon} - \rho \int_{\varepsilon_F}^{\infty} \frac{d\varepsilon'}{2\pi i} \frac{A(\varepsilon')}{\varepsilon' - \varepsilon} + \frac{1}{2} \gamma(\varepsilon) \quad \varepsilon < \varepsilon_F \quad (\text{A3.2})$$

$$\Gamma^-(\varepsilon) = \int_{-\infty}^{\varepsilon_F} \frac{d\varepsilon'}{2\pi i} \frac{\gamma(\varepsilon')}{\varepsilon' - \varepsilon} - \rho \int_{\varepsilon_F}^{\infty} \frac{d\varepsilon'}{2\pi i} \frac{A(\varepsilon')}{\varepsilon' - \varepsilon} - \frac{1}{2} \gamma(\varepsilon) \quad \varepsilon < \varepsilon_F \quad (\text{A3.3})$$

The integral equation (6.11) can then be written

$$\Gamma^+(\varepsilon) - \Gamma^-(\varepsilon) + i \tan \delta(\varepsilon) \{ \Gamma^+(\varepsilon) + \Gamma^-(\varepsilon) \} = 0 \quad (\text{A3.4})$$

or

$$\Gamma^+(\varepsilon) e^{i\delta(\varepsilon)} = \Gamma^-(\varepsilon) e^{-i\delta(\varepsilon)} \quad (\text{A3.5})$$

This relation immediately suggests the introduction of the function

$$\Phi(z) = \exp \left\{ \int_{-\infty}^{\epsilon_F} \frac{d\epsilon'}{\pi} \frac{\delta(\epsilon')}{\epsilon' - z} \right\} \quad (\text{A3.6})$$

which obviously is analytic everywhere except for a branch-cut along the real axis to the left of ϵ_F . This implies

$$\frac{\Phi^+(\epsilon)}{\Phi^-(\epsilon)} = e^{2i\delta(\epsilon)} \quad \epsilon < \epsilon_F \quad (\text{A3.7})$$

and, therefore, the function $\Gamma(z)\Phi(z)$ is continuous across the real axis to the left of ϵ_F . To the right of ϵ_F , however, it has a discontinuity across the axis of magnitude $-\rho A(\epsilon)\Phi(\epsilon)$. Thus, defining also the function

$$\Pi(z) = -\rho \int_{\epsilon_F}^{\infty} \frac{d\epsilon'}{2\pi i} \frac{A(\epsilon')\Phi(\epsilon')}{\epsilon' - z} \quad (\text{A3.8})$$

which obviously is analytic everywhere except at the discontinuity across the real axis to the right of ϵ_F , we see that the function $\Gamma(z)\Phi(z) - \Pi(z)$ is analytic everywhere. Since this function by virtue of the Eqs. (A3.1), (A3.6), and (A3.8) tends to zero at infinity it must vanish everywhere and we have

$$\Gamma(z) = \frac{\Pi(z)}{\Phi(z)} \quad (\text{A3.9})$$

Below the Fermi level ($\epsilon < \epsilon_F$) we can now obtain the solution $\gamma(\epsilon)$ to the integral equation (6.11) from the Eqs. (A3.2), (A3.3), (A3.9), and (A3.6). We have

$$\begin{aligned} \gamma(\epsilon) &= \Gamma^+(\epsilon) - \Gamma^-(\epsilon) = \Pi(\epsilon) \left\{ \frac{1}{\Phi^+(\epsilon)} - \frac{1}{\Phi^-(\epsilon)} \right\} = \\ &= \frac{\Pi(\epsilon)}{\Phi(\epsilon)} \left\{ e^{-i\delta(\epsilon)} - e^{i\delta(\epsilon)} \right\} = -2i \frac{\Pi(\epsilon)}{\Phi(\epsilon)} \sin\delta(\epsilon) \quad (\text{A3.10}) \end{aligned}$$

where the unsuperscripted functions on the real axis are obtained by replacing z by ϵ in the corresponding functions of a complex argument. Note that the function $\Pi(z)$ is continuous across the real axis below ϵ_F . The function $\Pi(\epsilon)$ turns out to vary rather slowly over the occupied band whereas both $\Phi(\epsilon)$ and $\sin\delta(\epsilon)$ can have appreciable structure. For instance, for strong core-hole potentials, the phase shift exhibits a resonant behavior towards the bottom of the band as does the TDOS in the presence of a core hole. In an attempt to make the structure of $\gamma(\epsilon)$ more apparent by eliminating the factor $\sin\delta(\epsilon)$ from Eq. (A3.10), we rewrite Eq. (A2.14) of Appendix 2,

$$A(\epsilon) + \frac{1}{\pi} \tan\delta(\epsilon) \int \frac{A(\epsilon') d\epsilon'}{\epsilon' - \epsilon} = - \frac{1}{V_0 \pi} \tan\delta(\epsilon) \quad (\text{A3.11})$$

Clearly this can be viewed as an integral equation that determines $A(\epsilon)$ if the phase shift $\delta(\epsilon)$ is known for all

energies. This equation is exactly of the same type as Eq (6.11) and we leave it to the interested reader to solve Eq. (A3.11) using the procedure demonstrated above in the case of Eq. (6.11). The result is

$$A(\varepsilon) = -\frac{1}{V_0 \pi} \sin \delta(\varepsilon) \exp \left\{ \frac{1}{\pi} \int \frac{\delta(\varepsilon') d\varepsilon'}{\varepsilon - \varepsilon'} \right\} \quad (\text{A3.12})$$

The expression

$$\eta(\varepsilon) = \exp \left\{ \frac{1}{\pi} \int_{\varepsilon_F}^{\infty} \frac{\delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' \right\} \quad (6.13)$$

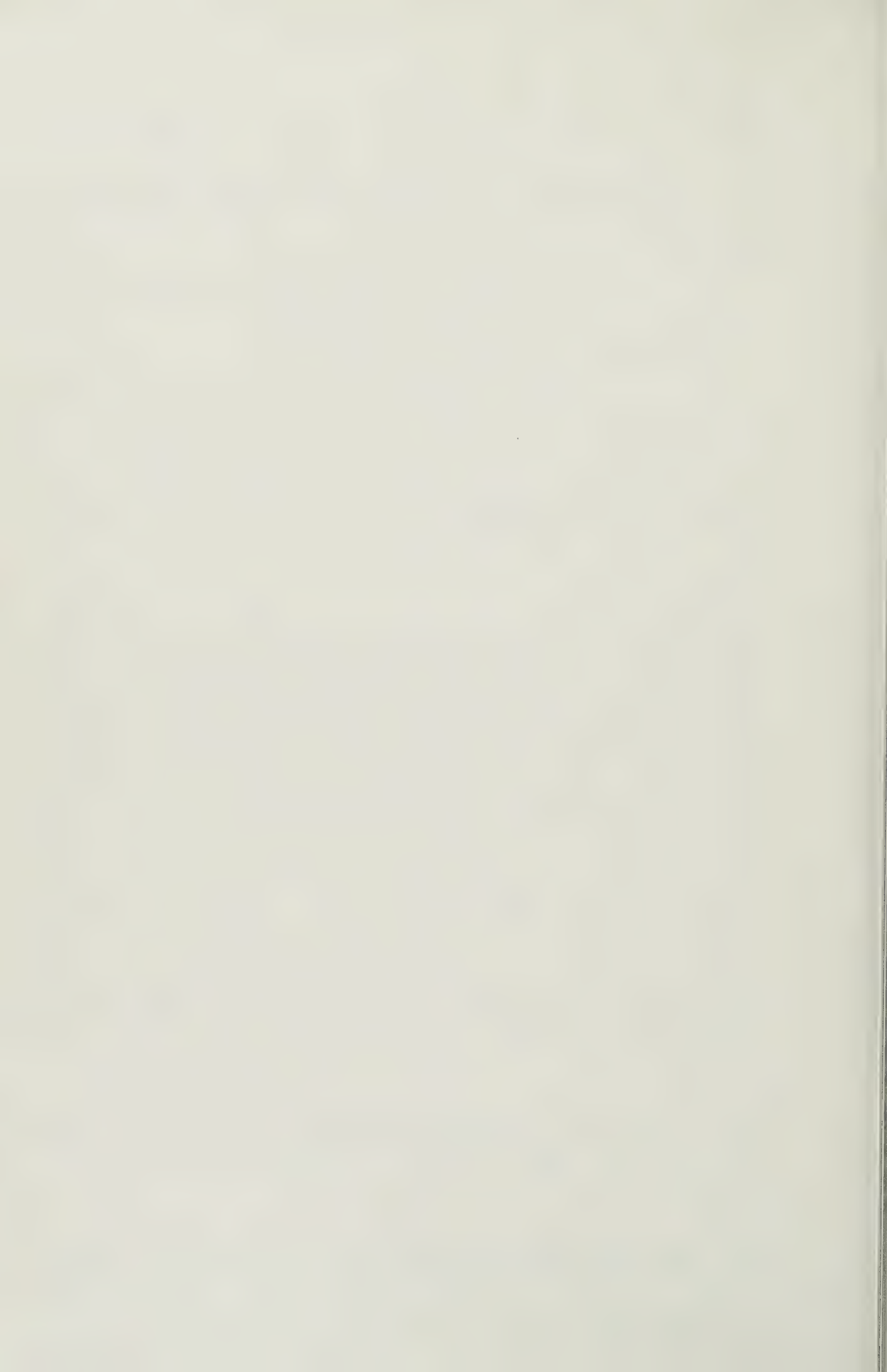
defining the function $\eta(\varepsilon)$, has a denominator which varies slowly for energies sufficiently below the Fermi level ε_F and we expect a slow variation over most of the occupied band also for $\eta(\varepsilon)$. Using the Eq. (A3.12) the function $\gamma(\varepsilon)$ can now be expressed in terms of $\eta(\varepsilon)$,

$$\gamma(\varepsilon) = 2\pi i V_0 \Pi(\varepsilon) \frac{A(\varepsilon)}{\eta(\varepsilon)} \quad (\text{A3.13})$$

Also the function $\Pi(\varepsilon)$ can be expressed in terms of $\eta(\varepsilon)$ to give

$$\Pi(\varepsilon) = \frac{1}{2\pi i V_0} \frac{\rho}{\pi} \int_{\varepsilon_F}^{\infty} \frac{\eta(\varepsilon') \sin \delta(\varepsilon')}{\varepsilon' - \varepsilon} d\varepsilon' \quad (\text{A3.14})$$

The last two equations give the Eq. (6.12) of the main text.



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43. In the ND model we introduce a statically screened potential into the free electron gas. From perturbation theory we obtain the second order contribution Δ_2^{ND} to the "relaxation" shift Δ_r of ND theory,

$$\Delta_2^{\text{ND}} = -(1/2) \int \chi_0(\underline{q}) |V(\underline{q})|^2 d^3q / (2\pi)^3.$$

Here, $\chi_0(\underline{q})$ is the static wave-vector dependent density response function of the free electron gas (the Lindhart function). In a more elaborate theory we introduce a bare core-hole potential, $w(\underline{r})$, into the interacting electron gas. There is then a linear term which is, however, cancelled by a term describing the core hole interacting with the positive background. The second order contribution, Δ_2 , to the relaxation shift is given by

$$\Delta_2 = -(1/2) \int \chi(\underline{q}) |w(\underline{q})|^2 d^3q / (2\pi)^3,$$

where $\chi(\underline{q})$ is the static density response function of the interacting electron gas and $w(\underline{q})$ is the Fourier transform of $w(\underline{r})$. In linear Hartree theory we have $V = w/\epsilon$ and $\chi = \chi_0/\epsilon$ giving

$$\Delta_2 = -(1/2) \int \chi_0(\underline{q}) |V(\underline{q})|^2 \epsilon(\underline{q}) d^3q / (2\pi)^3$$

where $\epsilon(\underline{q})$ is the static dielectric function. Thus, the ND result Δ_2^{ND} is clearly different from the correct result Δ_2 . This is a deficiency of the ND theory which need not concern us here, since we are only interested in line shapes and not in threshold positions.

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46. Due to an unphysical choice of potential in some cases discussed by Dow and Flynn³⁹ the states $|N, s \sim \rangle$ do not form a complete set and, consequently, the resulting spectrum does not fulfill the sum rule, Eq. (3.7)

47. Note that $V_{kk'} = V_o p_{ck}^* p_{ck'}$.

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51. The analysis in Sec. 6 suggests that the limit

$$\lim_{N \rightarrow \infty} | \langle N \sim | N \rangle |^{-2} J_1^{(N)}(\omega) \text{ is a reasonable}$$

choice for the spectrum $J_1(\omega)$. A similar definition can be chosen for the spectrum $J_2(\omega)$, etc.

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53. The energy variation of $C(\omega)$ for strong core-hole potentials is actually a spurious effect due to the fact that, for large threshold exponents α_o , the enhancement factor $(\epsilon_F / (\epsilon_F - \omega))^{\alpha_o}$ has a non-negligible energy variation also away from threshold. As shown in Sec. 6 this factor is more accurately given by an expression of the form $1 + a(\epsilon_F / (\epsilon_F - \omega))^{\alpha_o}$.

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55. Note that the spectrum d_2 is negative below the bottom of the band. This is no numerical artifact but is due to the fact that the spectrum obtained from the

transient Green's function only, i.e. by setting $\tilde{g}(t)=1$ in Eq. (2.27), is unphysical. Only the product $\tilde{g}(t)\tilde{G}(t;t)$ (Eq. (2.21)) has physical relevance.

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$$4\varepsilon_F$$

Table I. The integral $S = \int_0^{4\varepsilon_F} A_c(\omega) d\omega$ over the spectral function $A_c(\omega)$ from the finite-N approach is here shown as a function of N for two different square wells when no excitations (S_0), single pair excitations (S_1), and double pair excitations (S_2) are included in the sum over final states in Eq. (3.8)

$$\delta_F = 0.20 \pi$$

$$\delta_F = 0.41 \pi$$

N	S_0	S_1	S_2	S_0	S_1	S_2
40	0.914	0.995	0.997	0.676	0.971	0.994
80	0.902	0.994	0.997	0.637	0.955	0.994
150	0.891	0.992	0.997	0.604	0.937	0.993

Table II. Threshold Exponents and Broadenings Determined by Assuming Different Ranges of Validity of the Asymptotic Line Shape.

	s channel			p channel		
Fitting Range ^a	α	Γ_{Lor}	Γ_{Gau}	α	Γ_{Lor}	Γ_{Gau}
0.00 - 0.04	0.0336	0.00299	0.0233	0.0113	0.00300	0.0233
-0.04 - 0.04	0.0334	0.00300	0.0233	0.0112	0.00300	0.0233
-0.12 - 0.04	0.0338	0.00301	0.0233	0.0107	0.00299	0.0233
-0.20 - 0.04	0.0345	0.00297	0.0233	0.0102	0.00300	0.0233
exact values	0.0338	0.00300	0.0233	0.0111	0.00300	0.0233

a. The end points of the fitting region are given in Rydbergs relative to the threshold position.

Figure captions.

Figure 1. Comparison between the emission spectra obtained for a separable potential from the integral-equation formulation and from the determinantal finite-N approach ($N=80$).

Figure 2. The dynamical spectra (d) obtained in the finite-N approach for a spherical square-well potential (sq.w.) with radius r_c and a separable potential (sep) modeled to yield the same Fermi-level phase shift δ and the same integrated intensity of the static initial state spectrum (i). Also shown is the static final state spectrum (f).

Figure 3. Comparison between the dynamical spectrum obtained in the finite-N approach and the spectrum obtained from the Final State Rule, where C was determined by fitting to the dynamical spectrum over the threshold region.

Figure 4. Comparison between the dynamical spectra obtained in the finite-N approach for three square-well potentials with different radii r_c and whose depths were chosen to yield the same Fermi-level phase shifts $\delta_F = 0.9$. As the weights of the static initial state spectra differed, the dynamical spectra were, for easier comparison, scaled to have the same weights.

Figure 5. The dynamical spectra (full drawn curves) for three systems characterized by the same static initial state spectrum (heavily drawn, broken curve) with a bound state below the band and three different static final state spectra (dashed curves).

Figure 6. The dynamical (d) emission spectrum obtained in the finite-N approach ($N=80$) for a square-well potential is compared to the corresponding initial (i) and final (f) state spectra. The deviation from a horizontal line of the function $C(\omega)$ defined in Eq. (4.3) measures the deviation from the Final State Rule.

Figure 7. The dynamical (d) emission spectrum obtained in the finite-N approach ($N=80$) for a square-well potential is compared to the corresponding initial (i) and final (f) state spectra. The deviation from a horizontal line of the function $C(\omega)$ defined in Eq. (4.3) measures the deviation from the Final State Rule.

Figure 8. The dynamical (d) emission spectrum obtained in the finite-N approach ($N=150$) for a square-well potential is compared to the corresponding initial (i) and final (f) state spectra. The deviation from a horizontal line of the function $C(\omega)$ defined in Eq. (4.3) measures the deviation from the Final State Rule.

Figure 9. (a) Comparison between the dynamical $L_{2,3}$ emission spectrum for sodium (d, d_1, d_2) and the

static limits given by the initial (i) and final (f) state spectra. (d_2 - the threshold singularity is purely excitonic in nature, d_1 - the threshold singularity is reduced by particle-hole excitations of s-character, d - the threshold singularity is further reduced by particle-hole excitations also of p-character.

Figure 10. The exponent function $\alpha(\omega)$ obtained from the determinantal approach for $N = 100$ free s-electrons with a density corresponding to that of sodium.

Figure 11. The exponent functions $\alpha(\omega)$ obtained from the integral-equation approach for a model system with 5 separable potentials of different strengths. The Fermi energy is taken to be half the bandwidth of a semi-elliptic DOS.

Figure 12. The exponent function $\alpha(\omega)$ for a system chosen to model sodium. Also shown is the decomposition into individual angular momentum channels.

Figure 13. Comparison between the emission spectra obtained for a separable potential from the integral-equation approach and from the approximate expression 6.14.



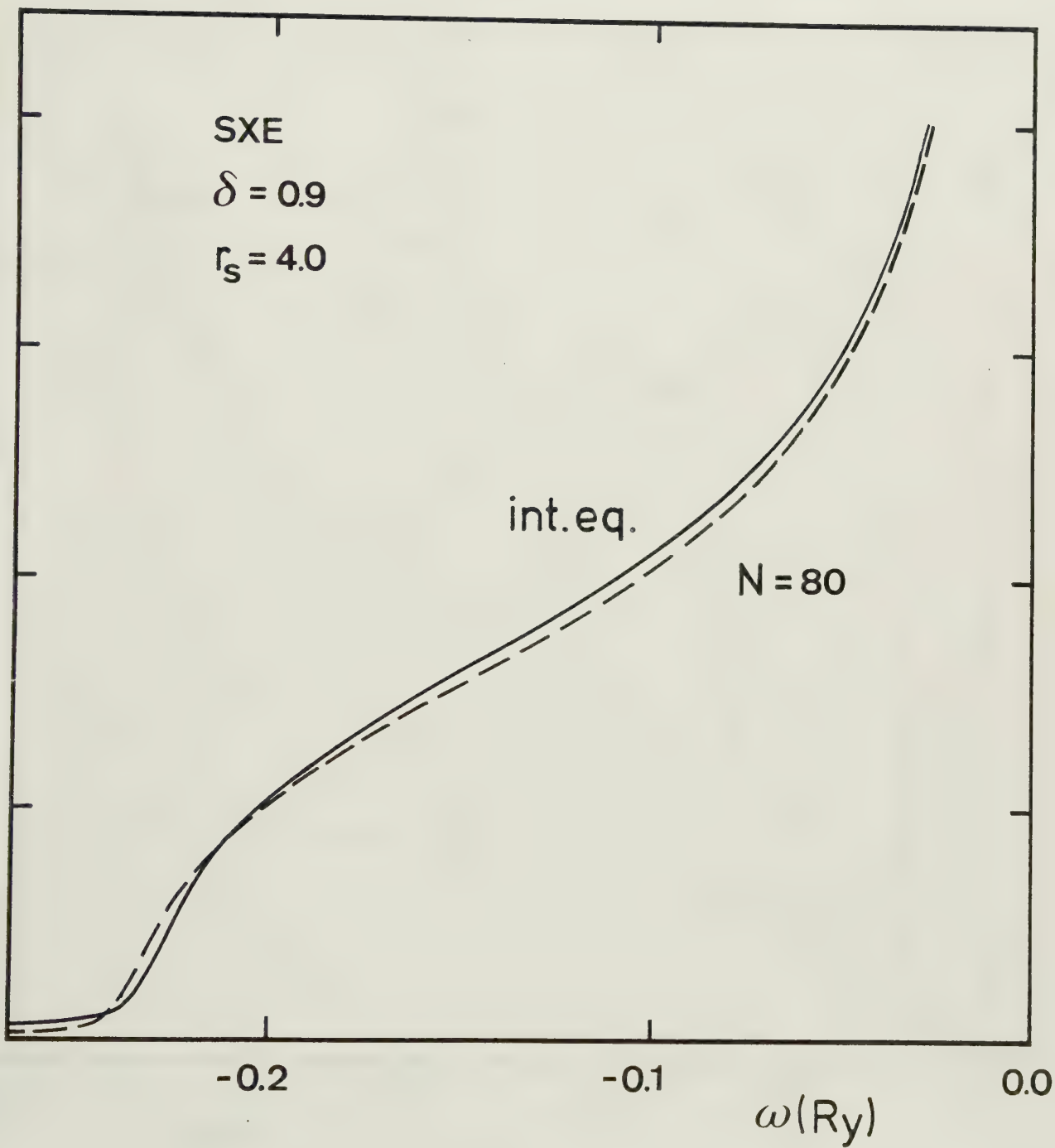


FIGURE 1

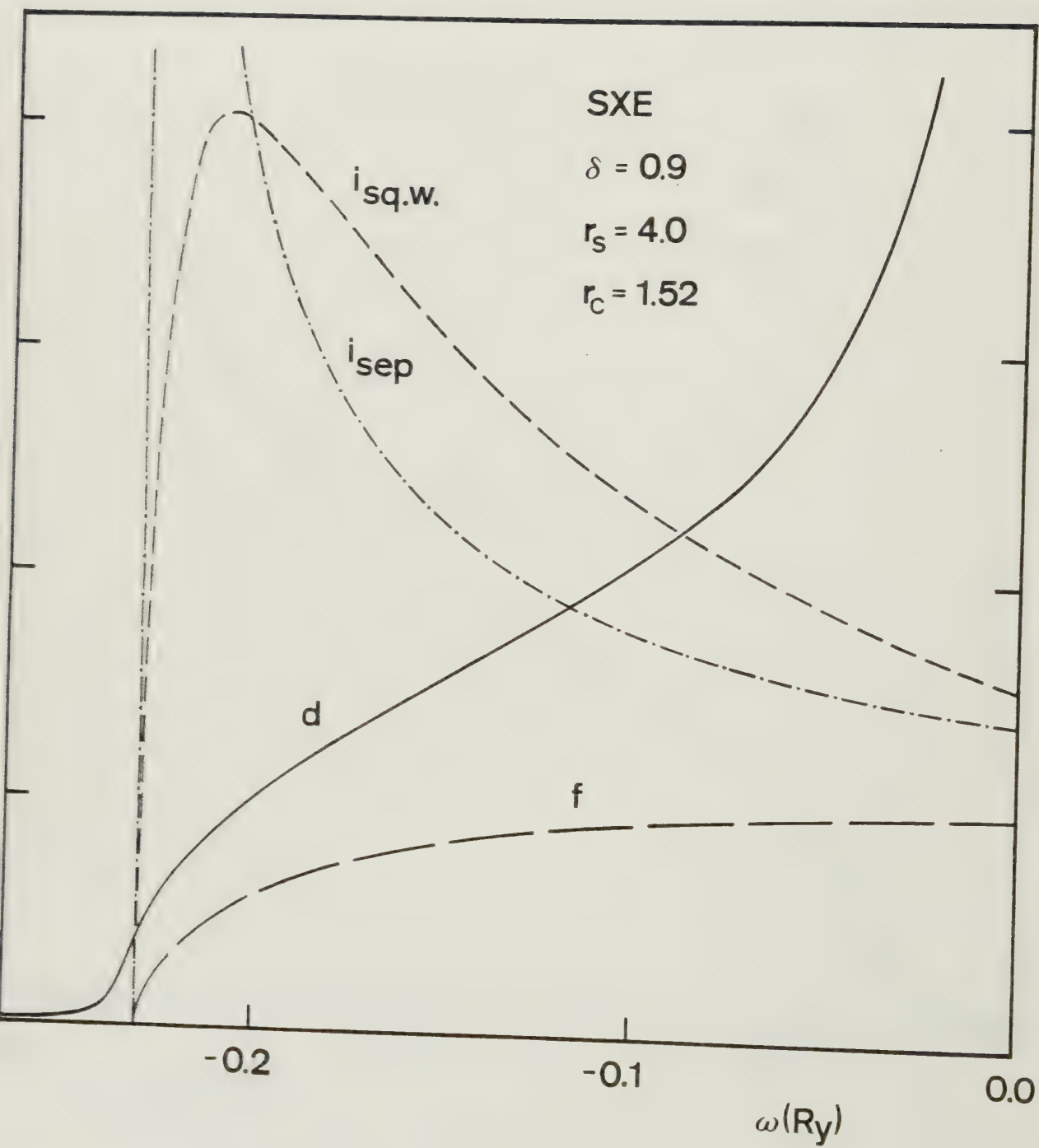


FIGURE 2

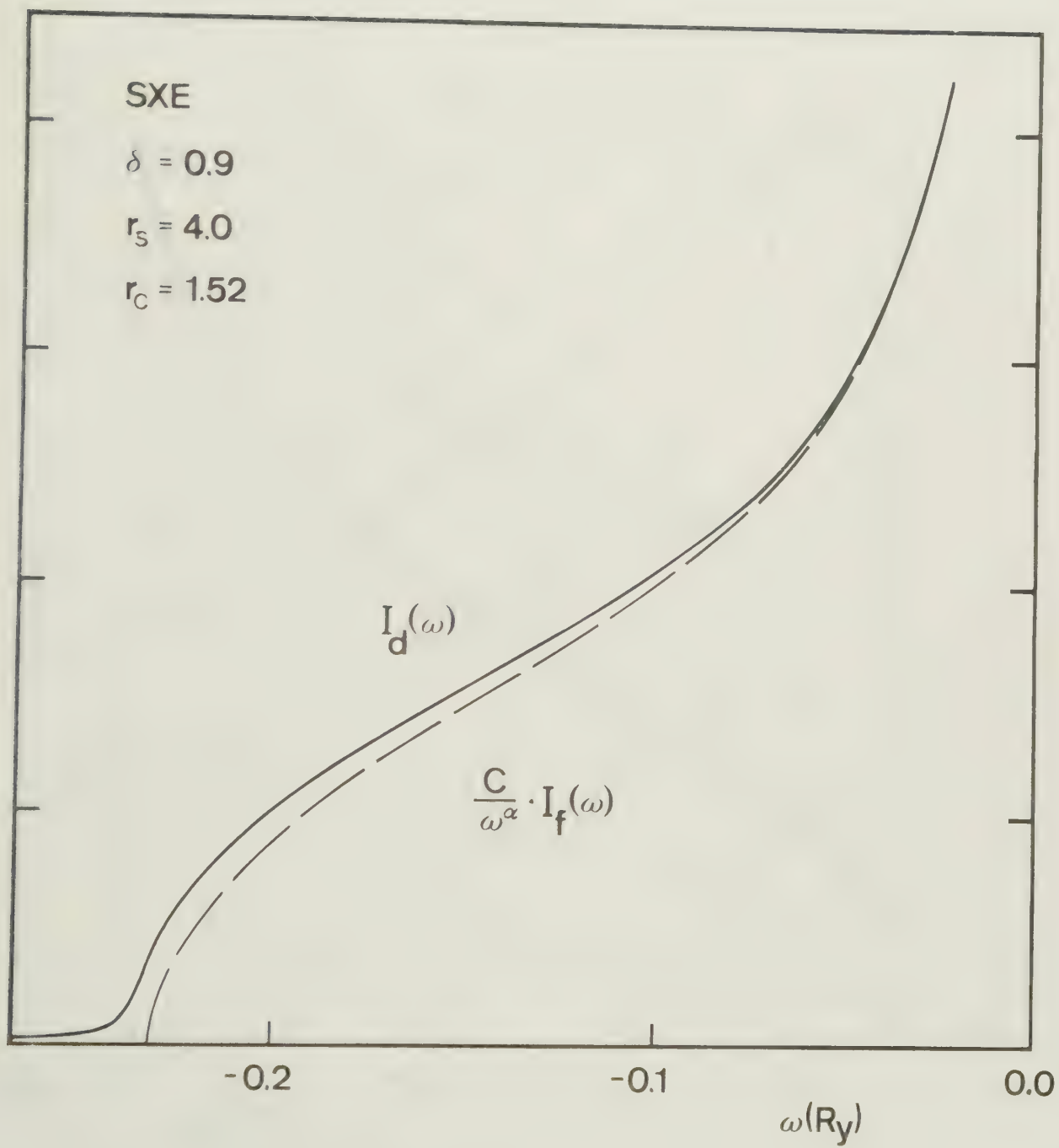


FIGURE 3

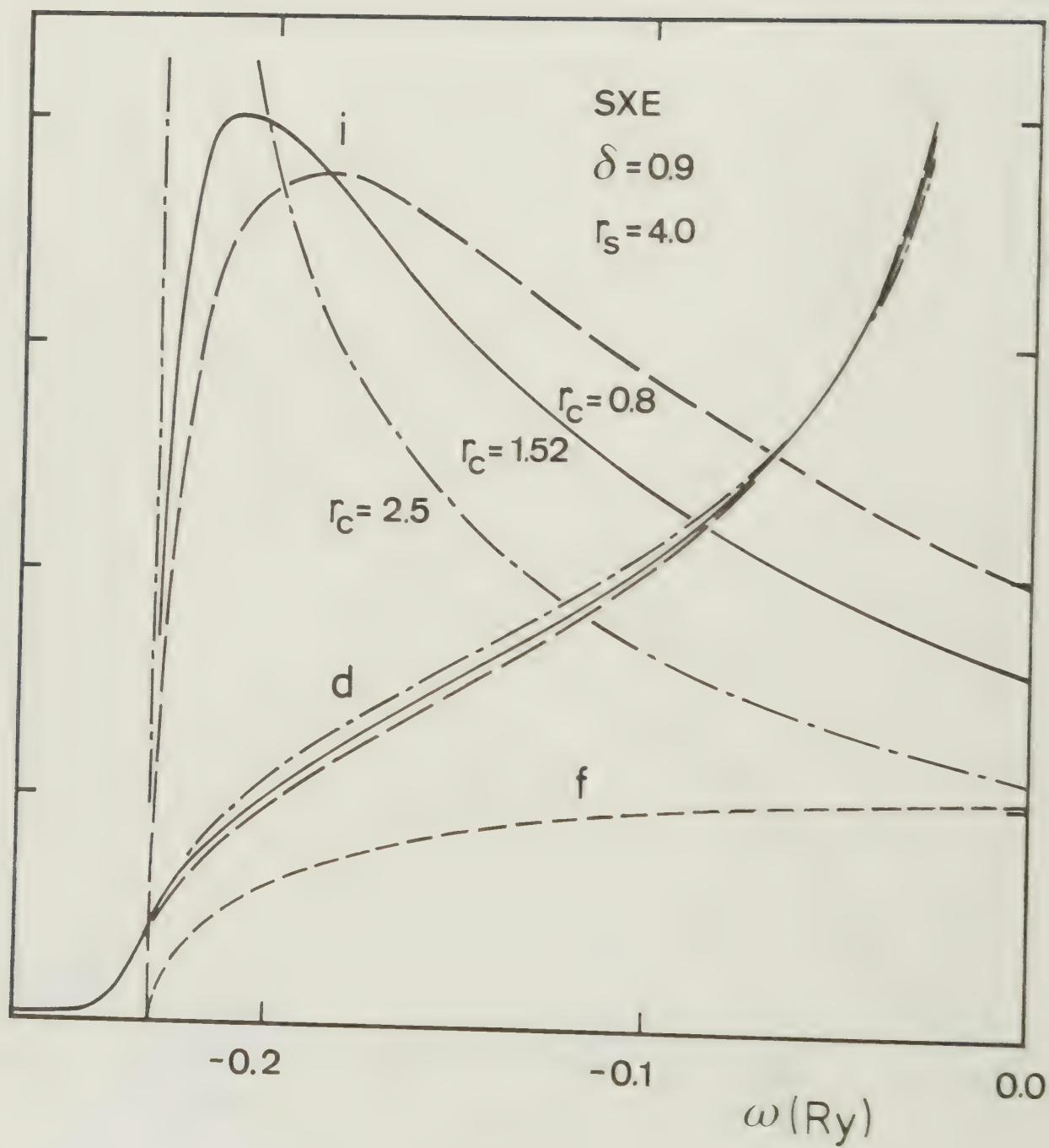


FIGURE 4

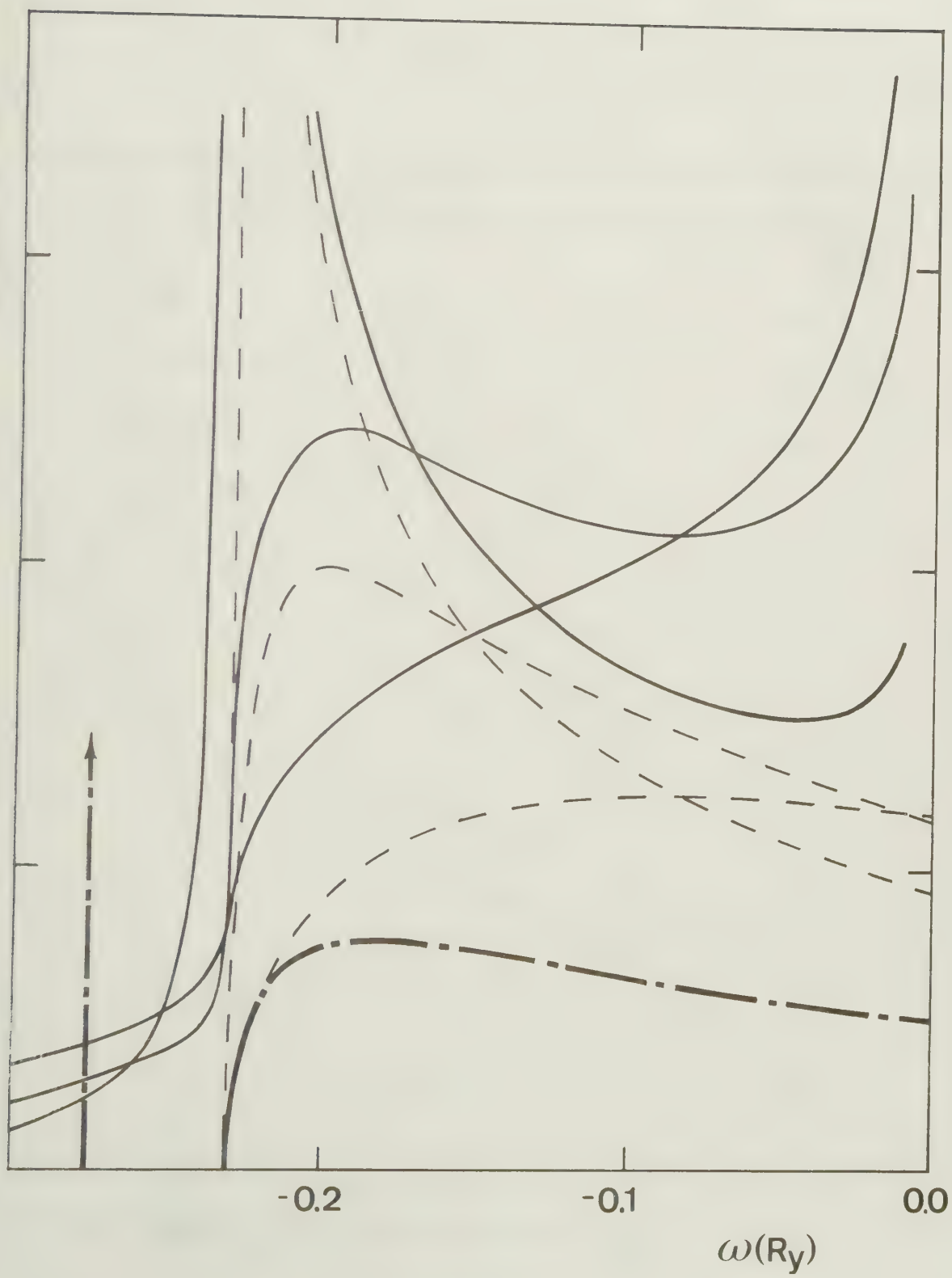


FIGURE 5

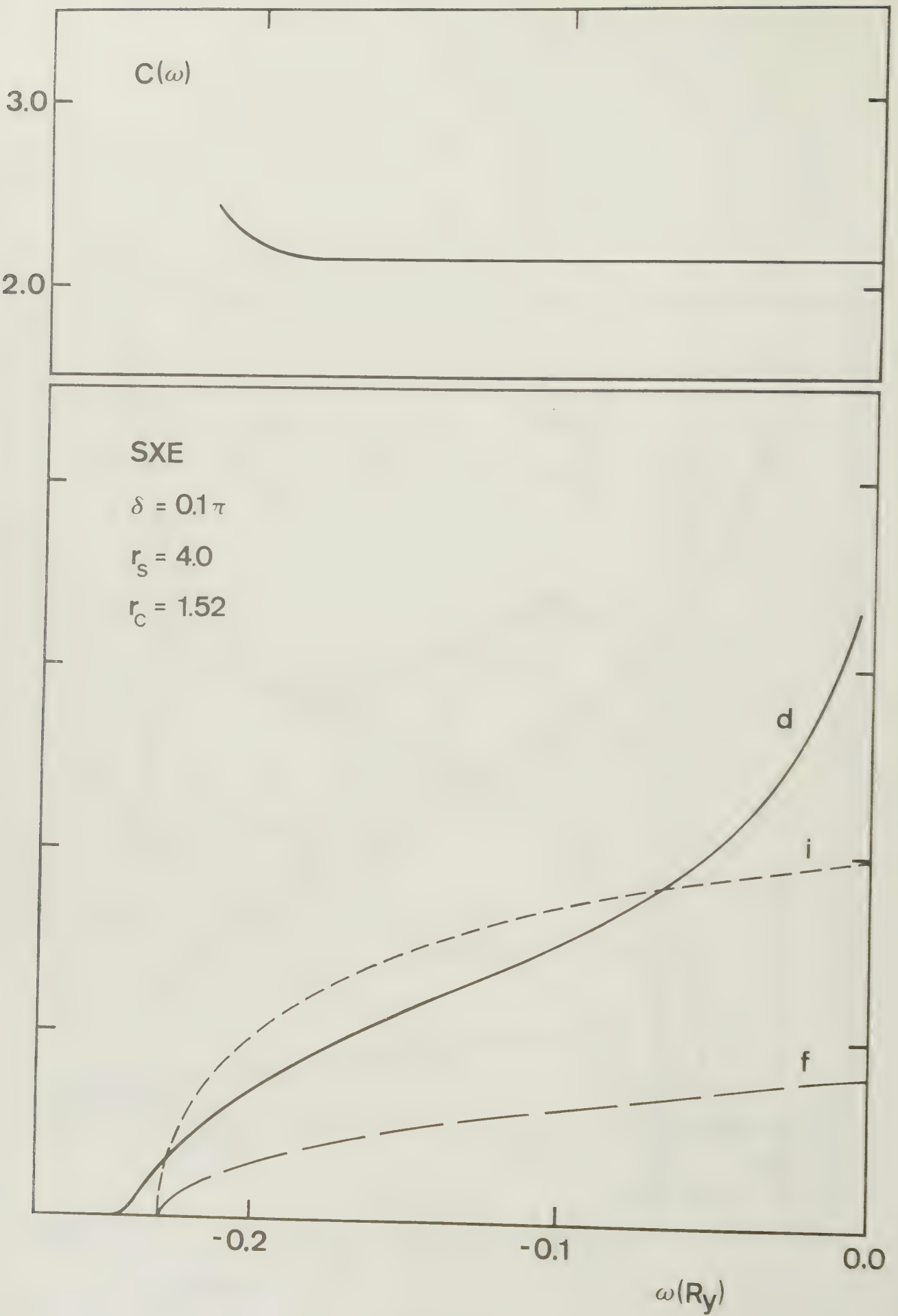


FIGURE 6

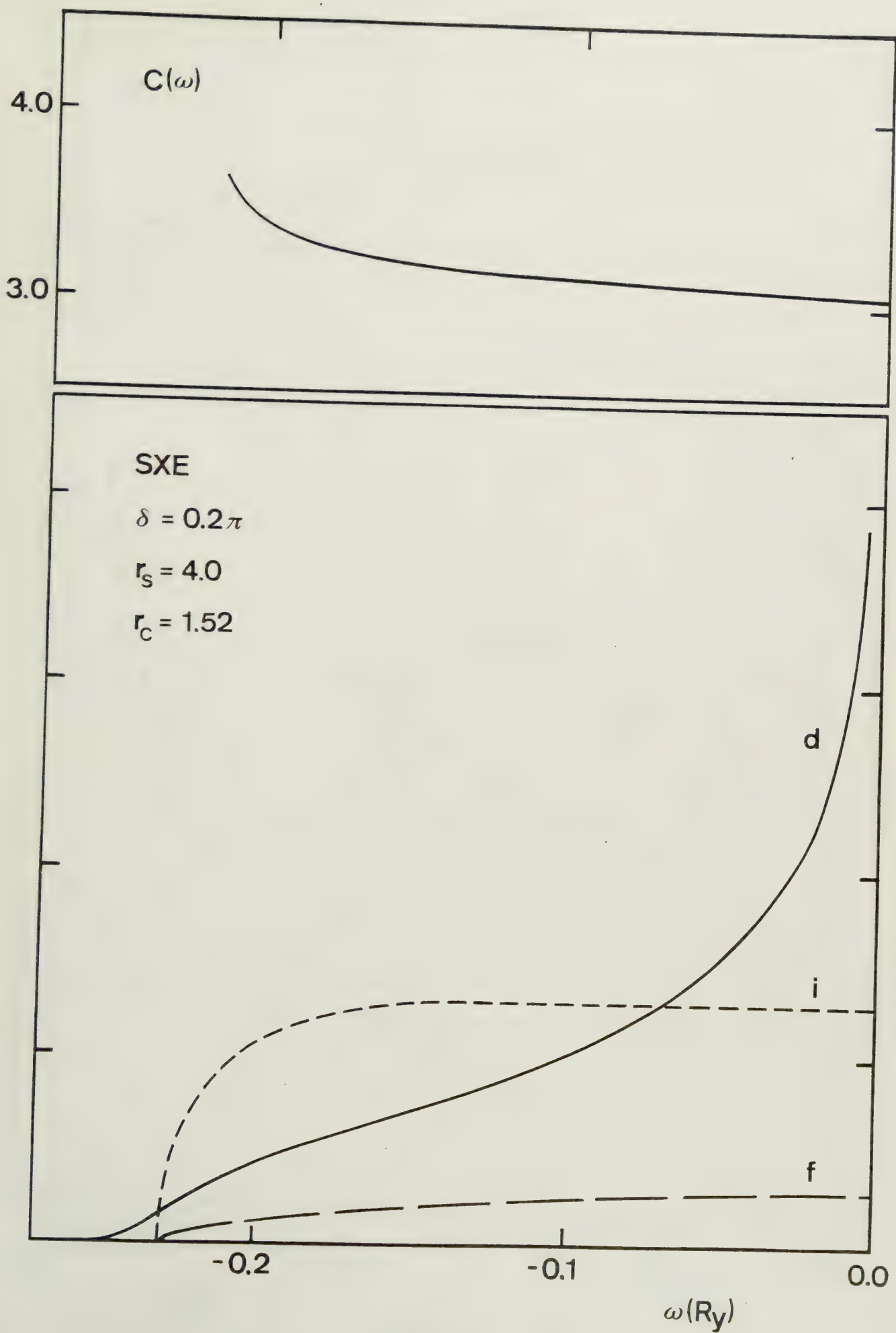


FIGURE 7

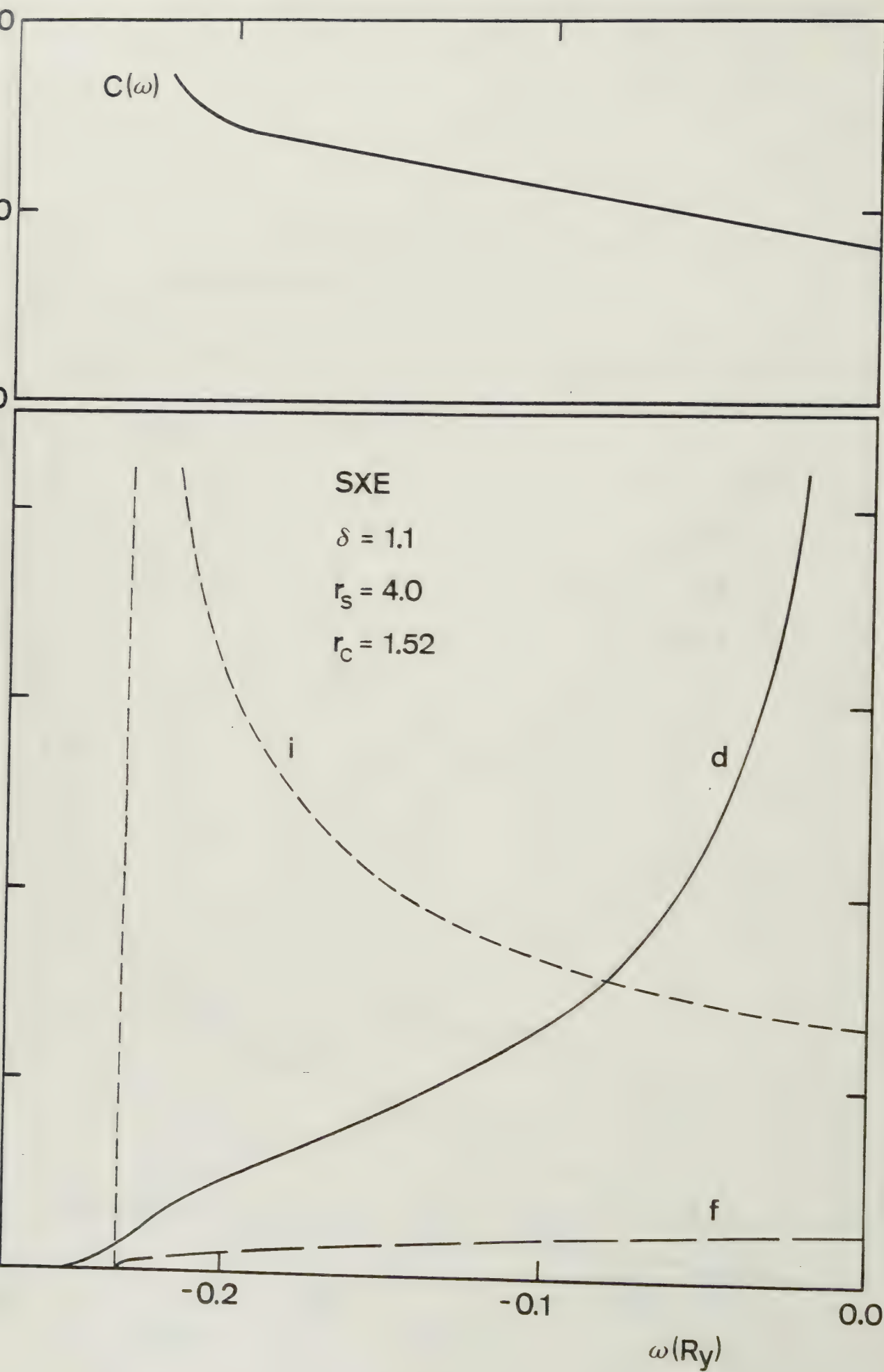


FIGURE 8

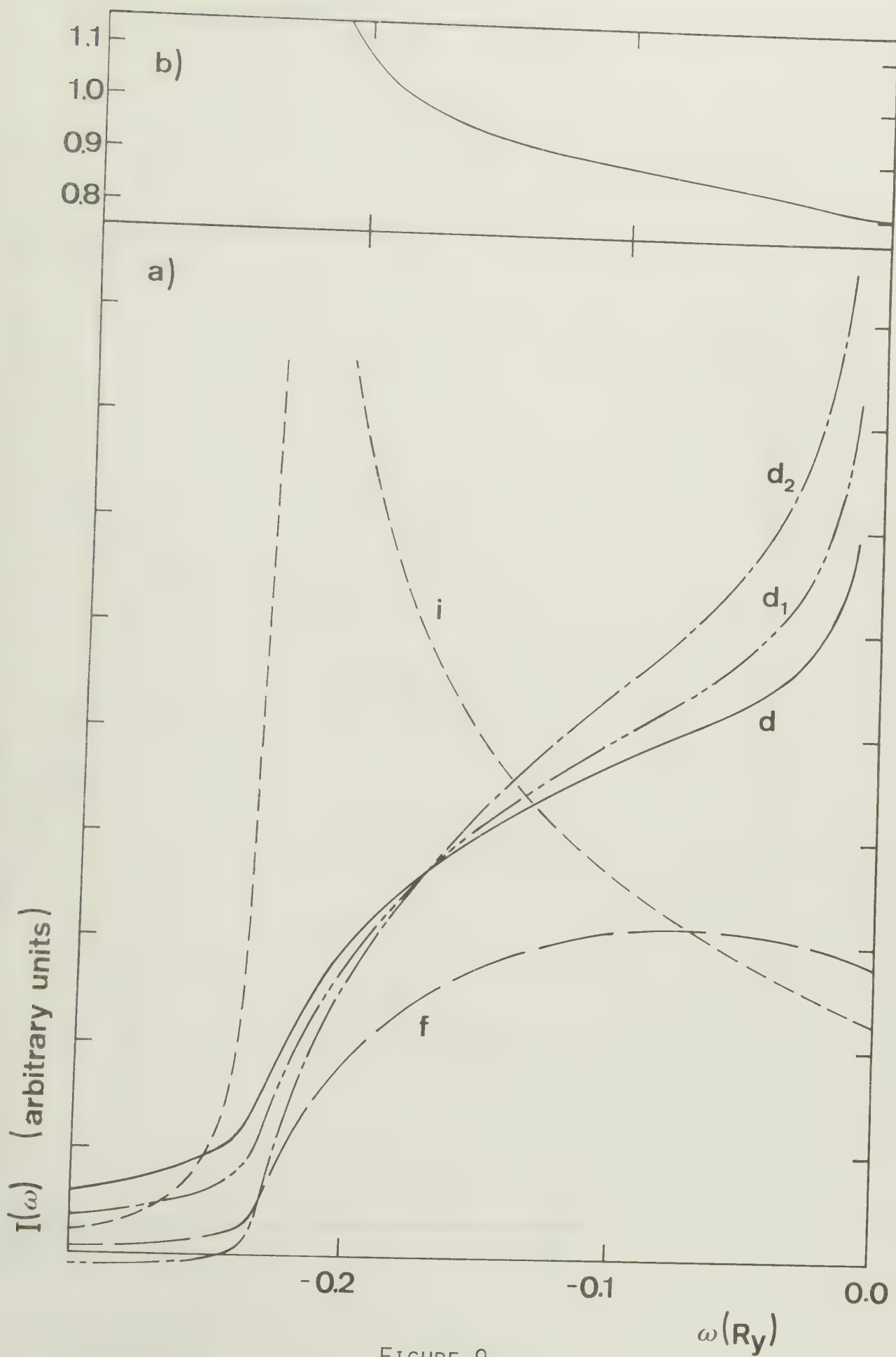


FIGURE 9

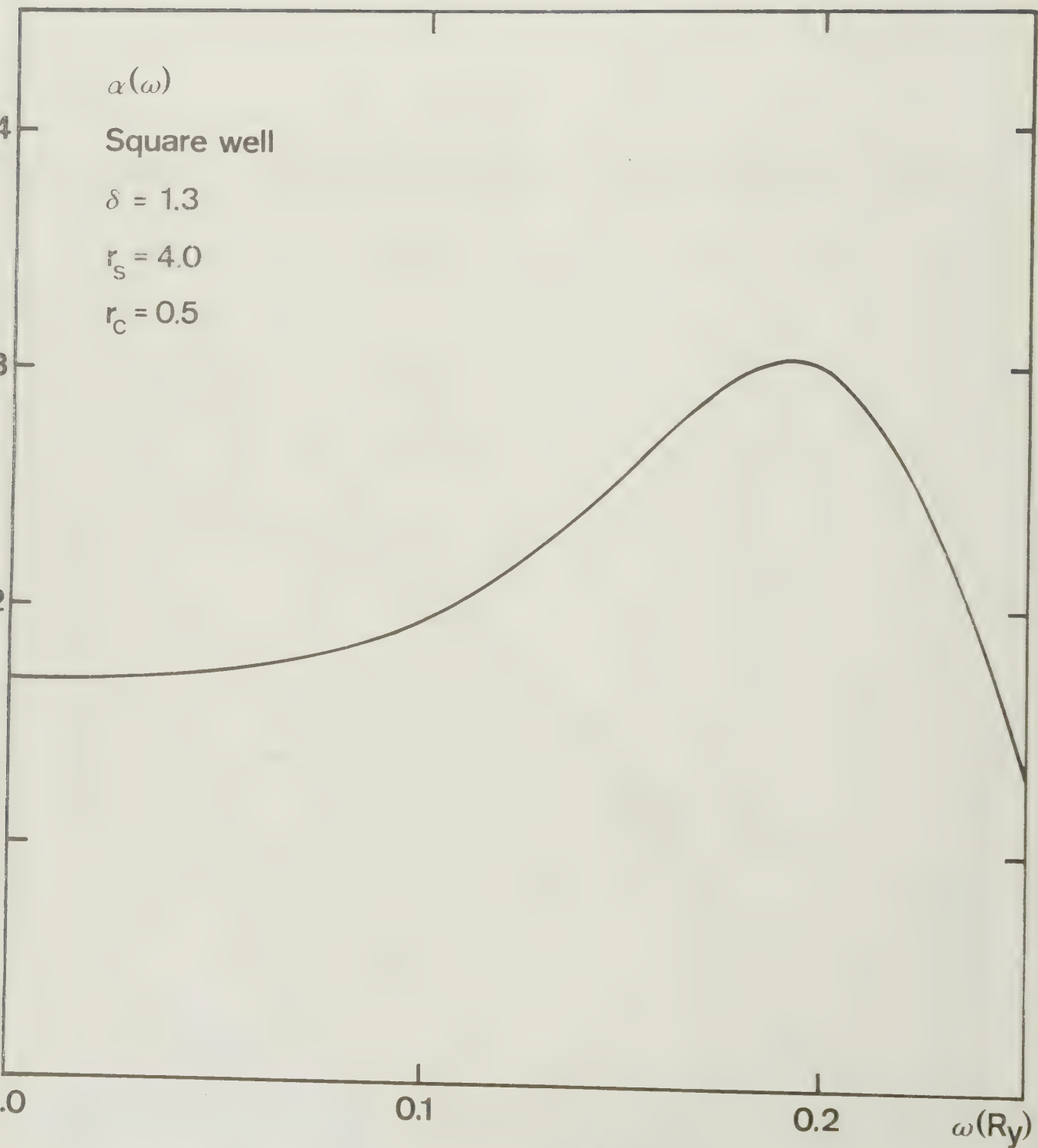


FIGURE 10

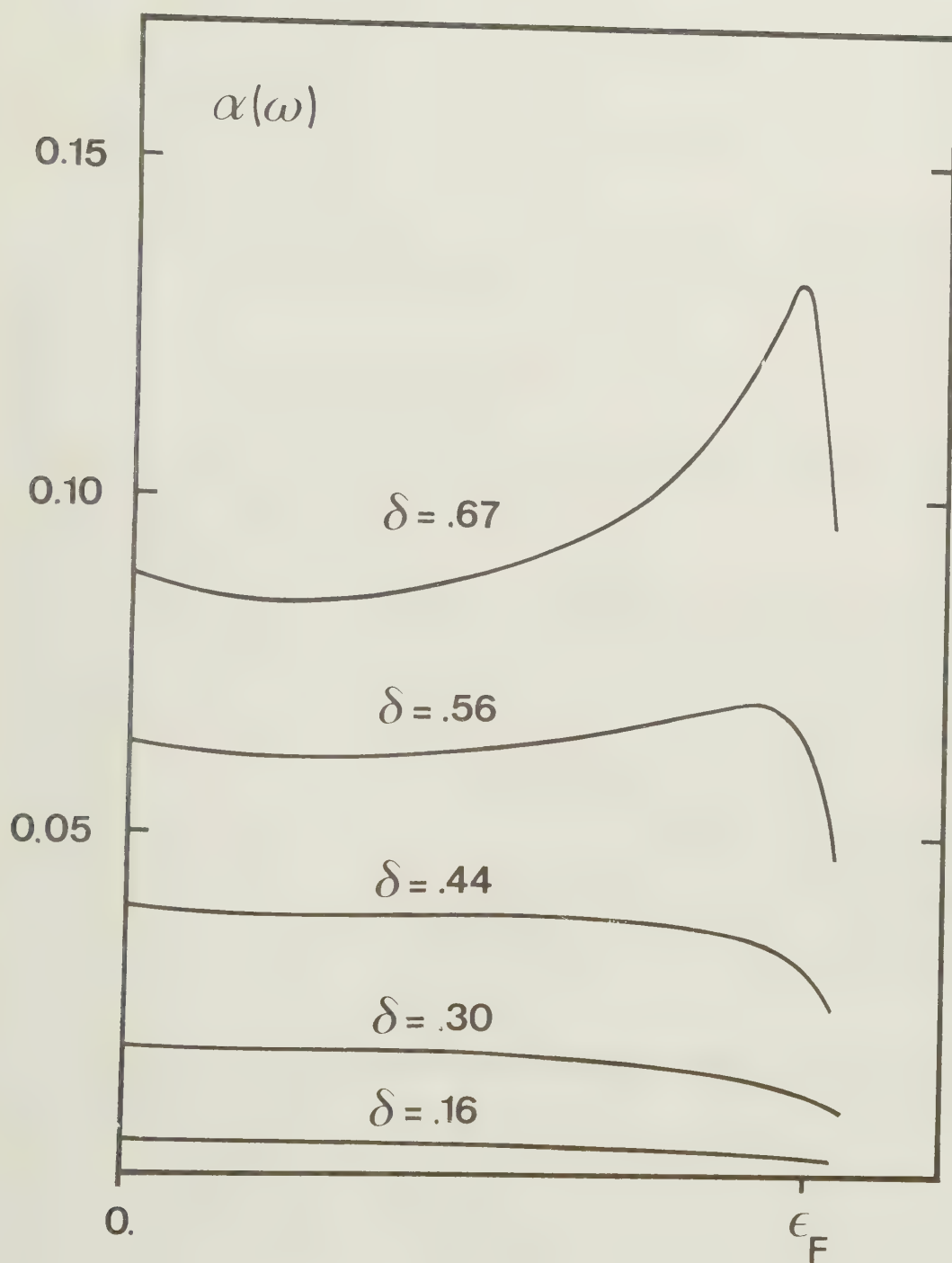


FIGURE 11

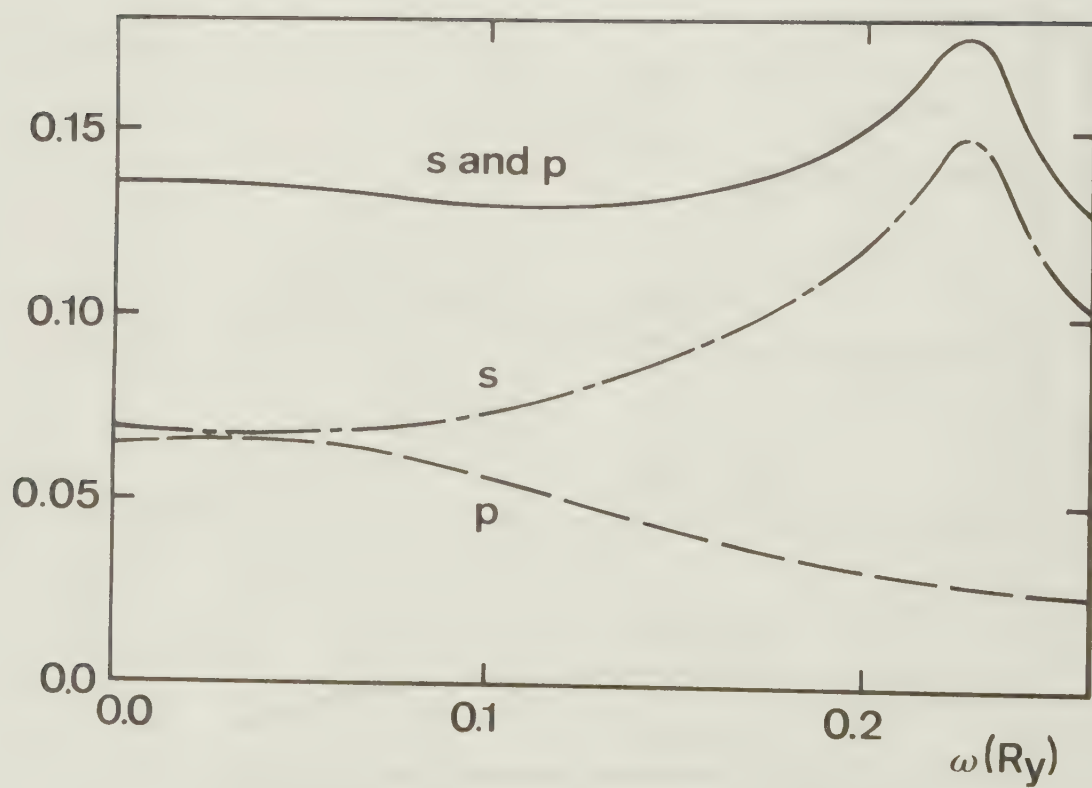


FIGURE 12

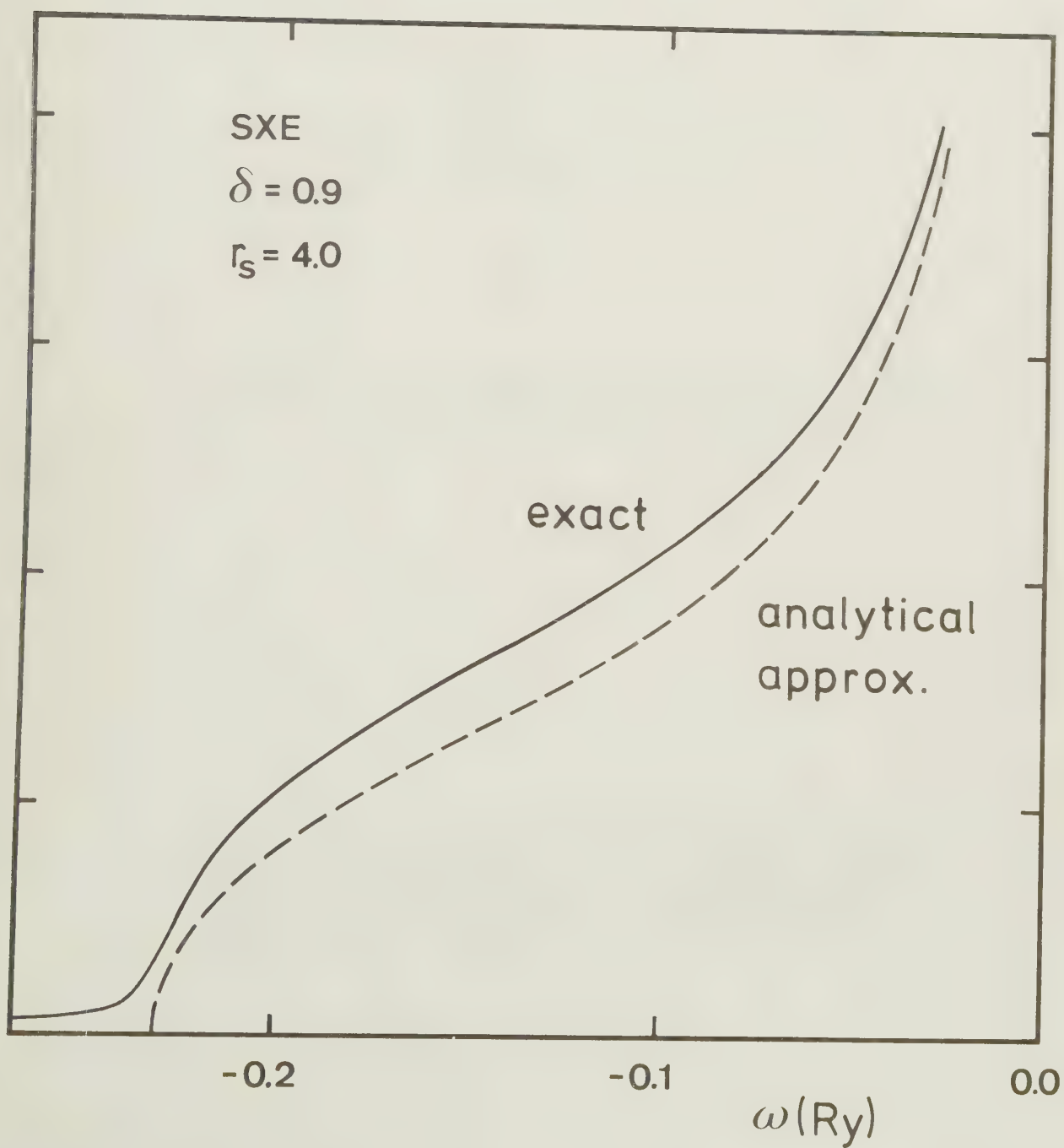


FIGURE 13



Investigations of
Core-Hole Effects in X-ray and Auger Spectra
of Simple Metals.

by

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Thesis for the degree of Doctor of Philosophy
(Avhandling för doktorsexamen)

To be presented, with the permission of the
Faculty of Mathematics and Natural Sciences
of the University of Lund, for public criti-
zism in the Auditorium of the Department of
Theoretical Physics on May 15th, 1981, at
1.15 p.m.

This thesis is based on the following publications:

- A. Ulf von Barth and Günter Grossmann: The Effect of the Core Hole on X-ray Emission Spectra in Simple Metals, Solid State Communications 32, 645 (1979)
- B. Ulf von Barth and Günter Grossmann: Dynamical Calculations of X-ray Absorption and Emission Spectra, Physica Scripta 21, 580 (1980)
- C. Ulf von Barth and Günter Grossmann: Static and Dynamical Effects of Core Holes in KLV Auger, SXE, and SXA Spectra of Simple Metals, submitted to the Physical Review.
- D. Ulf von Barth and Günter Grossmann: Dynamical Effects in X-ray Spectra and the Final State Rule, to be published.

The Sunbeam ... passing through a Glass Prism to the opposite Wall, exhibited there a Spectrum of divers colours.

Newton

INTRODUCTION

About two hundred years after Newton first analysed white light into its components of different colors, using the refractive properties of a simple prism, the methods of spectrum analysis had been refined, and spectroscopy, based on the interaction between light and matter had become a powerfull tool for the exploration of matter. When gaseous elements were caused to emit light, it was found that each element produced a characteristic line spectrum, i.e. the distribution of the emitted radiation was not continuous, but rather yielded a distinct pattern of many sharp, well-defined colors or frequencies. Once line spectra had been associated with all the elements known at the time, one could determine the chemical composition of a substance by identifying the individual elemental patterns in the composite spectrum. The discovery of new, previously unknown lines in the spectrum of a substance being examined would consequently also indicate the presence of a new element. Furthermore, it was found that gases would absorb light of a certain color only if the corresponding frequency also appeared in their emission spectrum. In this way one had devised an extremely reliable experimental technique for fingerprinting the elements, and it had become possible even to

chemically analyze distant objects, such as the sun and the stars, by merely investigating the radiation they emitted.

Soon conspicuous regularities were noted in the line spectra of many elements, but an understanding of the wealth of experimental information only became possible on the basis of a new theory, quantum mechanics, that was developed during the first decades of this century. The varying optical properties of the elements could now be explained in terms of a single parameter Z , the number of positively charged protons in an atomic nucleus - or the equal number of electrons contained in an atom. Within each atom, which was the fundamental building block of every element, the negatively charged electrons were found to be bound to the positive nucleus in stationary states of well-defined energy. To a first approximation, in the one-particle picture, quantum mechanics predicts a series of shells around the nucleus, each shell containing a certain number of levels. Each of these single levels may then be occupied by at most one electron, in the ground state of the atom the electrons occupy the Z lowest consecutive energy levels. Electrons in the inner shells, the core of the atom, are rather tightly bound and well localized within the atom. The electrons in the outermost shell, on the other hand, are the ones that are most sensitive to the environment of the atom, they are responsible for the chemistry of the elements, and were consequently called valence electrons.

When an atom is exposed to electro-magnetic radiation, of which visible light is a special form over a limited frequency range, energy may be transferred from the radiation field to the atom, but only in certain discrete quanta $\hbar\omega$, called photons, where $\hbar$ is Planck's constant and ω the frequency of the radiation. If the photon energy exactly matches the energy difference of two levels, and the lower level is occupied by an electron while the upper of the two levels is empty, the photon may be absorbed, lifting the electron to the higher rung on the ladder of electronic states. As the electronic levels are discrete and non-uniformly scattered over the energy scale, this then is a highly selective process, from the absorbed frequencies (or "colors") one directly gains information on the electronic structure. Similarly, an emission process may occur if the atom has previously been excited, so that the electrons no longer successively occupy the lowest possible states. Then an electron can fall from a higher to a lower unoccupied level, the energy set free in the transition is again equal to the difference between energies of the two levels and may be emitted as a photon, which again will have a sharply defined frequency. Consequently, the electronic structure, which is the key for understanding the properties of the elements, may be mapped out very directly by studying optical absorption and emission spectra. As the spacings of the electronic levels vary widely, on the average decreasing towards higher energies, so do the transition energies and the corresponding photon energies. Visible light will only probe the states of the outer valence

electrons, to fathom the inner core levels one needs to go beyond the ultra violet to x-rays, whose photons carry far more energy.

When atoms join together to form solids, the interaction between the outer valence electrons broadens their sharp energy levels into bands of densely spaced levels, while the core electrons remain in their tightly bound, discrete shells. For macroscopic samples the energy distribution of the valence band levels becomes so dense that it may be taken to be continuous for all practical purposes. In some materials the valence electrons will fill one or more bands completely, leaving others empty. If the occupied and unoccupied bands are separated by energy gaps, we speak of semiconductors and insulators. In a metal, the valence band is only partially filled, from the bottom of the band up to the Fermi level. The valence electrons are free to move throughout the crystal and e.g. electrical conductivity becomes possible. In simple metals, the valence electrons seem to have lost most of their atomic properties, they rather behave like a gas of free, independent electrons, a fact which greatly facilitated the earlier theoretical understanding.

The optical properties of solids within the visible region of electro-magnetic radiation are again determined by the valence electrons, transitions between valence levels leading to absorption and emission, endowing solids with a wealth of colors for everyone to see. If enough energy is supplied, e.g. via the highly energetic photons

of x-rays, even core electrons may be excited to the empty states in the valence band above the Fermi level. For sufficiently high energies the electron may overcome the surface barrier and will be able to escape from the solid. Knowing the frequency of the impinging x-rays, and measuring the energy of the emitted electron outside the solid, this experiment, called x-ray photoemission (XPS), yields direct information on the position in energy of the initially occupied core level. Subsequently, the hole deep in the core may be filled either by a higher core electron, which results in a line spectrum, or by a valence electron. As the valence electrons are distributed continuously over the valence band, the resulting emission spectrum will also be continuous, its width directly reflecting the width of the occupied part of the valence band. The fact that a hole, once created, only lives for a finite period of time results in an uncertainty of its energy which, according to Heisenberg's uncertainty principle, is inversely proportional to its life time. The energy distribution of the emitted photons reflects this uncertainty in energy and the spectrum will be life-time broadened. As the broadening, to which also other factors contribute such as the experimental arrangements, limits the amount of information that may be extracted from the experimental spectra, it is advantageous to focus on those core levels that have the smallest life-time width. Generally, the life times decrease with increasing binding energies. One thus studies transitions to the higher core levels with binding energies in the range of about 30 - 300 electron Volts yielding photons on the low energy side

of the x-ray spectrum. These soft x-ray emission experiments (SXE) were first done in the thirties and strongly supported the early theories of metals. In the complementary absorption experiment (SXA), the incident x-rays will be absorbed by a core electron as soon as the photon energy suffices to lift the electron above the Fermi energy. The absorption spectrum thus exhibits a sharp threshold at the Fermi energy, higher frequencies exploring the structure of the unoccupied regions of the valence bands.

While these experiments have been of immense value for the development of an understanding of the solid state, it also has become apparent that the simple model outlined above is not able to account for the finer details of the experimental results. Emission and absorption spectra exhibit peaks at the Fermi edge, and the emission spectrum has a tail extending to lower energies. The spectrum of energies of the emitted electrons in XPS is not a single, discrete line, but rather has an asymmetric shape, the main peak being accompanied by further peaks at lower energy, so-called satellites. In order to understand these features, one can no longer consider the creation of a core hole on a certain atom of a solid in absorption or in XPS as a process only involving this particular electron and the radiation field. In fact, all electrons of the system experience a shock when the deep hole is created, as this is equivalent to suddenly adding a localized positive charge to the system. The valence electrons will be

attracted by the long-range Coulomb potential of the hole, and as they are very mobile, they will gather at the excited site until the additional negative charge they carry suffices to cancel the long-range, attractive field of the core hole. The core hole is said to be screened. What in the simplest picture is a one-electron effect becomes inextricably entangled with the simultaneous reaction of all other electrons. The shock of the core-hole creation may thus lead to excitations also of the other electrons, the outgoing electron in XPS, for instance, will have to share its energy with these excitations, its energy spectrum will reflect these losses and broaden from a single line to a continuous spectrum.

When a core hole is created, as e.g. in XPS or by electron bombardment, the hole in the inner shell may also be filled by an outer-shell electron without the simultaneous emission of a photon. The energy can instead be transferred to another electron that is excited to an unoccupied state of the valence band. If its energy is high enough, it will, as in XPS, escape from the solid and can be detected outside. This Auger process is the dominant mechanism that, in competition with radiative transitions, limits the life times of shallower core levels. If the electron filling the core hole originates in another sharp core level, the energy transferred to the emitted electron is well-defined and the analysis of its energy distribution will yield a direct map of the occupied states from which it was excited. The energy spectrum will exhibit lines corresponding to core levels

and broader bands which reflect the occupied part of the valence band. The latter features are called core-core-valence (CCV) Auger spectra. The information they provide is complementary to that obtained in SXE, but again, attempts to reconcile the shapes of the spectra obtained from the two experiments have shown that one must go beyond the simpler models. The many-electron effects, which are due to the presence of core holes and which are shown to be essential for a detailed understanding of both the x-ray spectra and the CCV Auger spectra of simple metals are the subject matter of the present thesis.

SUMMARY OF PAPERS

The first paper (A) examines the theoretical description of soft x-ray emission spectra, and the question is raised what effect the presence of the core hole in the initial state of the x-ray transition will have on these spectra. In the one-particle picture the emission spectrum is simply related to the transition density of states (TDOS), which in turn is determined by the density of states and the transition matrix elements. On the one hand one may choose to neglect the core hole altogether, as has generally been done in previous calculations, and rely on bandstructure calculations for the perfect periodic solid to obtain the TDOS. On the other hand one can explicitly include the static, screened core-hole potential in the calculation, i.e. obtain the TDOS from a rather more involved impurity calculation for a solid with a core hole on one site. Calculations for both these static limits for the $L_{2,3}$ emission in sodium are reported and it is found that the two resulting spectra differ drastically. In $L_{2,3}$ emission the initial state hole is located in the 2p shell and due to the selection rules for optical dipole transitions, this experiment probes valence electrons of angular momentum

$l = 0$ and 2 character (s and d). The static effect of a self-consistently screened core hole is shown to be very strong, leading to a marked enhancement of the state density of s electrons near the bottom of the band. The spectrum obtained by including the core hole thus shows a pronounced peak near the bottom of the band, no trace of this effect is, however, seen in experiment. Experiment instead agrees well with the result obtained by disregarding the core hole entirely. As both approaches are equally valid within the one-particle picture, this discrepancy indicates the necessity of going beyond one-particle theory for a theoretical interpretation of emission spectra.

A theory that accounts for the interaction between the valence electrons and the core hole and also for the fact that the core hole is annihilated during the x-ray emission process had been presented by Nozieres and DeDominicis (ND)¹. This theory thus incorporates the essential dynamics of the process, namely the switching-off of the core-hole potential acting on the valence electrons. The interactions between valence electrons, e.g. dynamical screening effects, are, however, neglected. From a preliminary numerical evaluation of ND theory for a model system chosen to simulate sodium, it is found that the overall shape of this dynamical spectrum is closely given by the static one-particle result corresponding to the final state, which in emission has no core hole. The fact that the spectrum based on a bandstructure calculation agrees with experiment and the result of the

analysis of ND theory are then summarized in the rule of thumb that emission spectra will reflect the spectral properties of the final state.

This Final State Rule is then successfully applied to give the first theoretical interpretation for the shape of the sodium $L_{2,3}$ satellite emission spectrum. This high energy satellite is produced by transitions that fill one of two initially created core holes in the 2p shell. According to the Final State Rule, the satellite spectrum should be obtained from one-particle wave functions calculated in the presence of one core hole. The agreement between the theoretical result obtained in this way and experiment is gratifying, the spectrum does exhibit the full, strong static effect of one core hole, while the dynamical effect of the second hole being annihilated again does not affect the overall shape of the spectrum.

Corresponding calculations were also done for lithium yielding results very similar to those of sodium. From both calculations it is apparent that the valence electrons of p symmetry ($\ell = 1$) are much less affected by the core hole than the s electrons, in that the shape of their spectral distribution remains almost unchanged. Due to the dipole selection rules the p electrons are probed in K emission from lithium and our results in combination with the Final State Rule enable us to explain the observed similarity between the main band and the satellite emission spectra.

The second paper (B) reports detailed dynamical calculations based on ND theory for various model systems that show the Final State Rule to be well satisfied in all cases considered. The analysis is extended to absorption spectra, where again the spectra are found to reflect the spectral properties of the final state, which now for absorption does include a core hole. In their original paper, Nozieres and DeDominicis had evaluated their theory asymptotically to predict a singular behaviour of the emission and absorption spectra at the Fermi edge. From the dynamical calculations it is found that this behavior can be well accounted for by simply multiplying the static final state spectrum by a power-law factor, whose exponent, as predicted by ND, is determined by the Fermi-level phase shifts of the core-hole potential. The validity of this asymptotic behavior can thus be extended to finite energies, a result that justifies the commonly used procedure to obtain the threshold exponents by fitting to experiment over a finite energy region near the edge. Similarly, the asymptotic ND theory predicts a power-law singularity for the shape of the XPS line. We also investigate over what range this asymptotic behavior may be expected to be valid. It is found that although the calculated shape may deviate somewhat from the asymptotic result, the asymmetry index, according to ND again related to the Fermi-level phase shifts, may still be obtained with sufficient accuracy by fitting the full result with a power-law line shape.

The third paper (C) is in part an extended version of paper A. A detailed account is given of the repeated-cluster calculations that were used to obtain the self-consistently screened core-hole potential and the corresponding one-particle wave-functions. The sodium $L_{2,3}$ emission spectra are recalculated, now also to include the threshold singularity via multiplicative factors. In the satellite spectrum this feature is rather effectively obscured by the strong broadening, in the main band it becomes essential for the fit to experiment. The detailed agreement, however, requires an exponent much smaller than the value predicted by the Fermi-level phase shifts deduced from XPS experiments. This discrepancy suggests that with regard to the detailed edge behavior the present theory of x-ray spectra may have to be refined.

The investigation of core-hole effects is then extended to the recently reported KLV Auger spectra of simple metals. In this case the initial hole is located in the 1s shell (K) while the final state has one hole in the 2s or 2p shell (L) and another in the valence band (V). These spectra were surprising in that they showed "mystery" peaks which seemed to be inconsistent with the results of SXE. Although the core holes of the initial and final states are located in different shells, their effect on the valence electrons will, according to the equivalent core approximation, be rather similar. In any case, a small dynamical effect associated with a possible small change in potential would pass unnoticed as the broadening of the experimental spectrum is rather large. More

important in this case is, however, the fact that both initial and final states contain a core hole. The strong static effect of the core hole evident from our calculations should thus be clearly seen in the spectra. On the basis of the KLV spectra calculated for sodium we are in fact able to explain the hitherto mysterious structure seen at the bottom of the band, by attributing it to the core hole distorting the spectral distribution of s electrons. In fact, the KL_1V spectrum that is found largely to reflect the s electrons of the valence band is very similar in shape to the $L_{2,3}$ satellite, a strong indication for the common origin of the low energy peak. The paper ends with a discussion of the implications that our impurity calculations and the Final State Rule have for the interpretation of the alloy spectra of simple metals.

The fourth paper (D) explores the accuracy of the Final State Rule and provides further numerical evidence for its validity. Furthermore, a detailed theoretical background for the calculation of dynamical spectra is given. Our earlier results were based on the original integral-equation formulation presented by Nozieres and DeDominicis¹, which pertains to an infinite system and which for computational convenience relies on the use of a separable core-hole potential. We compare this approach to an alternative approach² based on a finite number of particles within a finite volume and demonstrate that this method gives accurate results already for a relatively small number of particles. While it is more difficult to

extract the exact threshold behavior from this determinantal method, it has the advantages of greater simplicity and of being able to treat arbitrary core-hole potentials with equal ease. This method thus allows us to compare results for separable and local potentials and it can be concluded that separable potentials do not give rise to any spurious results and that they may be used successfully to model realistic core-hole potentials. Finally, also an approximate theoretical treatment is presented which may be solved analytically and which provides insight into the mechanisms that lead to the Final State Rule. This treatment also lends support to the procedure of including the edge singularity via simple multiplicative factors.

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NOTE:

